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REVIEW OF PRIOR STUDIES OF FUEL EFFECTS ON VEHICLE EMISSIONS

August, 2008

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Final Report

Review of Prior Studies of Fuel Effects on Vehicle Emissions

CRC Project E-84

August, 2008

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1. EXECUTIVE SUMMARY

This report was prepared under contract to the Coordinating Research Council (CRC) in fulfillment of Project E-84. It provides a summary of the technical literature describing the effects of fuel composition on exhaust emissions of gasoline and diesel vehicles in on-road and off-road applications. Extensive literature searches were carried out covering years since 1990 for gasoline vehicles, light-duty (LD) diesels and off-road engines/vehicles; and since 1998 for heavy-duty (HD) diesels. Abstracts were reviewed carefully and all relevant papers were obtained and read. The search revealed that significant research has been carried out in the U.S., Europe and Japan, along with some research in other regions.

Directional changes for gasoline vehicles are summarized in the table below. Deciding which changes to consider for regulatory purposes requires knowledge of environmental needs, a detailed description of the vehicle fleet and a modeling tool that will provide a quantitative estimate. Currently, the most complete model is the Predictive Model developed by ARB (California Air Resources Board).[1]

	To Reduce Gasoline Emissions, Make the Directional Changes Shown Below							
	Aromatics	Benzene	Olefins	Sulfur	Oxygenates	RVP	T_{50}	T_{90}
HC	↓	*	↑	↓	↑	↓	↓	↓
CO	↓	*	↑	↓	↑	↓	↓	↓
NOx	↑	*	↓	↓	↓	0	↑	↑
Toxics	↓	↓	↓	↓	#	*	↓	↓
PM	*	*	*	*	*	*	*	*
0 No effect								
* Data are lacking to estimate an effect								
# Data exist, but effect is variable								

Shown below are areas where existing data is sparse or non-existent and where additional research would be helpful in defining fuel effects. If new vehicle technology such as GDI (gasoline direct injection) is developed and implemented, additional data would be required with that technology.

- Effects of fuel parameters on PM emissions. Currently, this is not a particularly important area because gasoline vehicle PM emissions are still a small portion of the total inventory, but could become more important as diesel PM emissions drop.
- Effects of RVP on emissions at all temperature levels.
- Better understanding of the relative impacts of mid-fill volatility, back-end volatility and composition on exhaust emissions.
- Long-term effects of sulfur on aftertreatment components and exhaust emissions. This may not be relevant for U.S., Europe and Japan, where sulfur levels are extremely low, but could be important for other regions, as they consider future sulfur levels.

Significant data exist which relate diesel fuel properties and exhaust emissions, both for HD diesels and for HD diesels. In many cases, the conclusions are not consistent and may be contradictory.

The following table represents a summary of the current state of knowledge of the impact of fuel property changes on diesel exhaust emissions.

To Reduce Diesel Emissions, Make the Directional Changes Shown Below (Light Duty / Heavy Duty)						
Density	Cetane	Aromatics/PAH	Sulfur	Back-End	Fatty Acid Esters	Fischer Tropsch
HC ↓/*	↑/↑	↑/↓	0/0	0/↑	↑/↑	↑/↑
CO ↓/*	↑/↑	↑/*	0/0	0/↑	↑/↑	↑/↑
NOx */↓	*/*	↓/↓	0/0	#/#	↓/↓	#/↑
PM ↓/*	↓/#	↓/↓	↓/↓	↓/↓	↑/↑	↑/↑

0 - No effect

* - Data are lacking to define effect

- Data exist, but effect is variable

For existing LD and HD diesel technology, a full statistical analysis of existing data would help develop an understanding of quantitative effects of fuel parameters on exhaust emissions. This would be an update of the work published by EPA in 2001 [2]. An important piece of this effort would be an analysis of the ability to determine unambiguously the impacts of density, cetane and aromatics on emissions. Much of the published data, with a few notable exceptions, has confounded these parameters. If the analysis cannot determine independent effects, then additional experimental data would be useful.

Additional research on Fatty Acid Esters and Fischer Tropsch liquids would be helpful to determine their effects. This research should not use splash blending to prepare fuels, but should blend fuels so that the contribution of these blendstocks can be tied to specific properties. A key question, especially for Fatty Acid Esters is why they reduce emissions.

There is a need for research on diesels with exhaust aftertreatment. Future diesel engines will almost certainly contain some form of aftertreatment. When the technology is developed and implemented, research should be carried out to determine the impact of fuel variables on engines and vehicles containing the new technology. There is some existing data with oxidation catalysts in LD diesels and with diesel particulate filters (DPF) , but very little data with Urea-SCR (Selective Catalytic Reduction) and NSR (NOx Storage Reduction) systems.

Off-road mobile sources are a growing part of the total mobile source inventory, and stringent emissions standards are being implemented. Most research to date on this sector has evaluated new blendstocks, such as splash blended ethanol in gasoline or splash blended FT in diesel. Prediction of the impact of specific fuel blends is, therefore, very difficult. As advanced technology is applied to off-road mobile sources, new data should be developed in carefully planned programs to define the relationships _between fuel properties and exhaust emissions.

The following limitations of this analysis should be understood when evaluating the report's findings

- Many programs did not report the results of a statistical analysis, and did not report the statistical significance of the findings.

- Some programs that reported statistics did not present an evaluation of the Type II errors. That is, if no significant results were found, there is no way to tell if the test design was powerful enough to have seen a relatively large effect as statistically significant.

- Some programs tested a limited number of vehicles. Given the known variability in response among vehicles, it is difficult to make generalizations from a small sample.

- In some programs, the fuel properties were not independently varied, so it is not possible to assign results to fuel properties unambiguously. Many reports recognize this uncertainty, but some do not.
- Some research programs were designed to demonstrate the benefits of certain fuel formulations or fuel blendstocks, and the changes in emissions could not be assigned to any one or group of fuel properties.

2. INTRODUCTION

This report provides a summary of the literature describing the effects of fuel properties on emissions from on-road and off-road gasoline and diesel-powered vehicles. It is part of a project funded by the CRC Project E-84.

The Statement of Work issued by CRC is shown as Appendix I. For LD gasoline vehicles, the time period covered in this report dates to a similar review by Koehl et al. [3] of research up to 1989. The Koehl survey was one of the initial reports of the Auto/Oil Air Quality Improvement Research Program (AQIRP) and this report includes all AQIRP research along with other work through the end of 2007.

Research on diesel engines has been described separately for LD and HD diesels, for reasons discussed below. For HD diesel, the time period covered in this report dates from an extensive review published by Lee, Pedley and Hobbs [4] in 1998. Earlier research will be cited only when not covered by Lee. Other reviews have been published and these are also cited in this report. For LD diesel, not covered by Lee, research going back to 1990 was considered.

Off-road mobile sources comprise a wide variety of applications and literature is considered separately for spark ignition and compression ignitions engines. Research published since 1990 was considered for inclusion in the report. As will be described below, off-road emissions are subject to increasingly stringent emission standards and major reductions are either underway or are about to be implemented.

It should be recognized that the changes in technology in the last two decades is different for gasoline and diesel vehicles. For gasoline vehicles, technology changes have been largely evolutionary. While extraordinary improvements have been made in catalytic aftertreatment systems, fuel management and electronic engine controls, the basic elements of design have stayed constant:

- Feedback control of air/fuel ratio
- Port fuel injection
- Three-way catalysts (TWC)

One noteworthy technological addition is the use of on-board diagnostic (OBD) systems to monitor the operation of emission control systems and report malfunctions to the driver.

For diesel vehicles, changes have been revolutionary and have been driven in part by the imposition of stringent emission standards. Direct injection has almost totally replaced indirect injection, even for LD diesels. Fuel system and injection system pressures have risen continuously. Injection is controlled electronically and can be extremely complex consisting of multiple injection events. Catalytic emissions control aftertreatment systems are much more commonplace, and their use will be expanded further in the coming years. Overall, engine controls are becoming more sophisticated and consist of multiple feedback systems that adjust operating conditions as necessary to maintain low emissions and high efficiency.

A. ORGANIZATION OF REPORT

Gasoline vehicles, diesel vehicles and off-road mobile sources are considered separately; within each class of vehicle, the emissions impacts of individual fuel parameters are described. For gasoline vehicles, research programs are described chronologically within major geographic regions (U.S., Europe, Japan, other). At the end of each section, a summary provides general conclusions and highlights areas where the data may be inconsistent. With limited exceptions, only included is research that tested fully built vehicles on dynamometers using recognized emission test cycles such as US FTP (Federal Test Procedure), European MVEG or Japanese 10.15 mode test. Single cylinder engines tests and steady state testing were excluded.

For diesel vehicles, LD and HD research is considered separately for a number of reasons.

- Emission standards and test cycles are very different for the two classes
- Typical duty cycles are very different. HD vehicles operate at high loads a higher fraction of the time.
- Engine technology has been different for LD and HD diesels. For instance, direct injection has been introduced much earlier in HD engines. As technology advances, and emissions standards tighten, this technology gap is narrowing.
- Aftertreatment systems have been different for LD and HD diesels. Oxidation catalysts are more common on LD diesels, and urea-SCR control of NOx is more common on HD diesels.

For diesel vehicles, research is described chronologically, generally without consideration of where the work was carried out. There is less variability in technology across regions for diesels than for gasoline technology, and for LD diesels, more research has been done in Europe and Japan, where diesels are more prevalent in the marketplace. Research carried out on fully developed multi-cylinder engines using recognized emission cycles was considered. For LD diesels, this generally includes the same type of test cycle used for gasoline vehicles. For HD diesels, the test cycle may be a series of steady state modes, or a series of transient modes carried out on an engine dynamometer. Exceptions were made where the research helped elucidate a particular issue or question.

For off-road emissions, spark ignition engines and compression ignition engines are considered separately. Smaller engines are generally powered by gasoline spark ignition engines and larger applications are generally powered by compression ignition engines using petroleum diesel fuel. It is appropriate to consider off-road applications separately from on-road applications for a number of reasons:

- Advanced technology has not usually been applied to off-road sources.
- Duty cycles are different, and tend to contain more steady state operation.
- Engine size and power output cover a very broad range.

The report also identifies where research might be helpful in furthering the understanding of important issues. Research needs are based on an estimate of future technology directions, and the state of fuel composition. For instance, studying the effects of sulfur might be helpful, but future sulfur levels will be extremely low, and such information might not be particularly relevant for the U.S., Europe and Japan.

B. METHODOLOGY

The main sources of information for this report were two extensive databases maintained by the Society of Automotive Engineers (SAE). The SAE Global Mobility Database contains searchable data on publications necessary for this project. The TechSelect Database contains searchable information and full text for publications after 1996. Searches were also conducted of EPA, DOE and ARB databases for government publications and other information. Most research has been published in the SAE literature,

but a significant number of papers have been published elsewhere and these were generally referenced in one or more SAE papers or review articles or a number of excellent government agency reviews.

The searches were designed to be inclusive. In total, 215 gasoline abstracts, 457 diesel abstracts and 106 off-road abstracts were reviewed for relevance. Of these, 109 gasoline papers, 128 diesel papers and 18 off-road papers were read in full. Appendix III contains tables showing the numbers of vehicles and fuels tested in each category, for each major fuel parameter. The numbers presented in the tables are simple sums of the totals in each reference. No attempt was made to break down each program to determine which vehicles and fuels were used to determine each parameter's response. However, the tables provide the reader with general information concerning the amount of data available and how recently it was collected.

An Excel spreadsheet was prepared which contains summary information about all the studies referenced in this report, as well as the complete reference. The specific information is listed in Appendix III, and the spreadsheet itself is available from CRC (www.crcao.org). Using the spreadsheet, it is possible to determine the studies that have been carried out to evaluate any given fuel property in broad vehicle or engine categories.

C. PRESENTATION OF RESULTS

In general, the impacts of changing fuel properties on emissions are shown as percent change because many publications report results only in percentage terms, and stating changes as percentages allows a comparison of results across programs.

With a few exceptions, results are shown as presented in the original paper. In a few cases, minor calculations were carried out to be able to present the results in a meaningful manner.

Some difficulties still remain when comparing results among different studies, because:

- Fuel parameters changes are not common across studies, and reanalyzing the data in individual research to provide the results on a common basis is beyond the scope of this report.
- As emission levels drop significantly, small differences in mass emissions represent very large percentages, and changes that are not significant from an air quality perspective may appear very large.
- Vehicle response is known to vary greatly from car to car and from model to model. Unless a relatively large number of vehicles were tested, different results are to be expected.

Changes in the concentration of one fuel component necessarily imply equal changes in one or more other components. For instance, when the concentration of aromatics is reduced by 10%, the concentration of some other component must be increased by 10%. Usually, paraffins are the swing component, so that the actual meaning of "reducing aromatics" is "reducing aromatics and replacing them by paraffins." When the change in concentration is in the parts per million range, as is the case for sulfur, the changes in concentration of the other fuel components are not measurable and can be ignored.

D. CAVEATS

Advanced engine technology, such as HCCI (Homogeneous Charge Compression Ignition) engines, that is not commercially available was generally not included in this report. Design of these technologies is far from fixed, and little if any data has been collected on fuel effects. Data that have been collected might not be relevant for future commercial designs.

When analyzing the literature, comparing results, and trying to draw generalizations, a number of problems were encountered.

- Many programs did not report the results of a statistical analysis, nor the statistical significance of the findings.

- Some programs that reported statistics did not present an evaluation of the Type II errors. If no significant results were found, there is no way to tell if the test design was powerful enough to have seen a relatively large effect as statistically significant.

- Some programs tested a limited number of vehicles. Given the known variability in response among vehicles, it is difficult to make generalizations from a small sample.

- In some programs, the fuel properties are not independently varied, so it is not possible to assign results to fuel properties unambiguously. Many reports recognize this uncertainty..

- Some research programs were designed to demonstrate the benefits of certain fuel formulations or fuel blendstocks, and the changes in emissions could not be assigned to any one or group of fuel properties.

This report includes all data collected in well designed programs and points out any potential uncertainties in the design or the analysis. Even programs for which there is limited ability to draw unambiguous conclusions can be used in a broader meta analysis of emissions data. Such a meta analysis is essentially what was done in developing various emissions models such as the EPA Complex Model and the ARB Predictive Model for gasoline.

3. GASOLINE

Emissions data on gasoline vehicles is organized according to fuel properties. Within each fuel properties, the literature is summarized first for the U.S. and then for Europe, Japan and other regions of the world. Almost all the data covers passenger cars, other LD vehicles, and some motorcycles and other two-wheeled vehicles.

Various driving cycles have been used to measure exhaust emissions from LD vehicles. In the U.S., the FTP75 has been used for many years, and has been supplemented in recent years by the US06, which represents more aggressive, high speed driving, and the SC03 which measures emissions under conditions when air conditioning is used. In Europe, the UDC (Urban Driving Cycle) and EUDC (Extra-Urban Driving Cycle) measure emissions under a variety of driving conditions including cold start. In Japan the steady state 10.15 mode test was used for many years and has been supplanted by the JC08 test, which has many similarities to the U.S. and European driving cycles.

Not much research has been carried out on the differences in fuel effects when measured on the different test cycles. It appears that the results are similar, especially where the test cycle includes cold start operation. It is beyond the scope of this report to analyze these differences, and for the purposes of this analysis, differences in test cycles have generally not been considered.

A. SULFUR

From an exhaust emissions perspective, sulfur concentration is probably the most important gasoline property. Present in trace amounts, sulfur does not contribute to octane or other vehicle performance attributes, yet it impacts operation of TWC and other components of modern emission control systems. Reducing the amount of sulfur in gasoline requires investment in new equipment and additional refinery operating expenses. Reducing sulfur concentrations in the refinery consumes energy and hydrogen, production of which can reduce the total amount of hydrocarbons available to blend into fuel. Reducing sulfur also increases refinery CO_2 emissions and can negatively affect fuel properties such as octane.

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Prior to AQIRP, initiated in 1989, there was little published research on the impact of sulfur. Furey and Monroe[5] studied one 1979 car with a TWC and Williamson et al. [6] studied aging in a laboratory setting. AQIRP carried out a number of large, well-designed programs to evaluate sulfur effects over a wide range of concentrations in different technology vehicles.

In the first AQIRP study, Benson et al. [7] tested ten 1989 vehicles with two fuels containing 49 ppm and 466 ppm sulfur, with results shown below:

	Change in Emissions 466 ppm S → 49 ppm S		
	HC	CO	NO$_x$
g/mi	-0.38	-0.362	-0.49
%	-16.1	-12.9	-9.0

Emission changes were highly significant (>>95% confidence level), although there was considerable car-to-car variability in response. The effect was virtually instantaneous – occurring within 10 miles – and fully reversible.

AQIRP tested these same ten vehicles in two subsequent phases, first with 5 fuels between 44 and 443 ppm sulfur, and then with 3 fuels varying between 11 and 50 ppm sulfur [8]. The objective was to test the linearity of the response and to measure toxics in addition to HC, CO and NO$_x$. Overall results are summarized below:

Percent Change in Emissions For Change in Sulfur		
	450 ppm → 50 ppm	50 ppm → 10 ppm
NMHC	- 17.2	- 6.6
CO	- 18.7	- 10.3
NO$_x$	- 8.0	NS
Benzene	- 20.8	- 11.8
1,3 Butadiene	NS	NS
Formaldehyde	+ 45	NS
Acetaldehyde	- 34	NS
NS: Not Statistically Significant		

There was a suggestion that the NMHC response was non-linear, although the significance level was only 85%. Specific reactivity using the MIR (Maximum Incremental Reactivity) scale increased by 8.4% when sulfur was reduced from 450 to 50 ppm. MIR is a calculated estimate of the amount of ozone produced by a compound or mixture of compounds under specific atmospheric conditions. It is used by ARB to develop comparisons of the relative ozone formation of emissions from different sources or from different fuels.[9]

Knepper et al. [10] reported on an AQIRP study with seven high emitters that found no impact of sulfur between 40 and 440 ppm on exhaust HC and CO, and a 12% reduction in NO$_x$. These results are consistent with vehicles that are running rich. Since the oxidation function of the TWC is severely inhibited, changes in sulfur have little impact on HC and CO. While running rich, the catalysts still retain the ability to reduce NO$_x$ and sulfur does have an impact.

As part of a larger program, Takei et al. [11] tested one vehicle calibrated to ARB standards of 0.25 g NMHC/mi. Both fresh and aged catalysts were tested. There was some suggestion that the sulfur

effect was not fully reversible, although the test protocol was not discussed in detail. Results are summarized below.

Percent Reduction in Emissions 300 ppm → 30 ppm Sulfur			
	HC	CO	NO$_x$
Fresh Catalyst	-33%	-15%	-37%
Aged Catalyst	-15%	-19%	-20%

Takei et al. [12] also tested a 1992 California Camry (0.25 g NMHC/mi standard) on fuels with low sulfur (10 ppm or 20 ppm) and higher sulfur (300 ppm) and reported a significant effect on NMOG, and no impact on specific reactivity (g O$_3$/g NMOG), but did not report statistics of these conclusions. No results were reported for CO and NO$_x$ emissions.

Hirota et al. [13] tested a 1991 Nissan Sentra on four fuels having sulfur concentrations of 10 ppm to 300 ppm and reported that TOG (Total Organic Gases), CO, and NO$_x$ decreased, although specific reactivity was not affected. No statistics were reported or discussed.

EPA [14] tested 20 normal emitters (1987-1990) and 16 high emitters (1986-1990) which were recruited at a state inspection station. Results comparing two fuels with 371 ppm and 112 ppm sulfur are shown below. These values were calculated from data in the paper.

	Percent Change in Emissions, 371 ppm → 112 ppm Sulfur					
Fleet	NMHC	CO	NO$_x$	Benzene	Formaldehyde	Acetaldehyde
Normal Emitters	- 4.7	- 8.7	- 7.2	- 6.5	+ 11.8	+ 3.7
High Emitters	- 5.2	+ 1.8	- 7.7	+ 0.4	+ 2.6	- 12.4

Considering the smaller sulfur change, these results appear to be consistent with AQIRP normal emitters, although there appear to be differences with the AQIRP high emitter results. In the report, statistical analysis was presented for a different comparison, so it is not possible to state the statistics for the results presented here.

In an effort to evaluate the EPA Complex Model, EPA tested ten vehicles (1983-1990 model year) on three fuels having sulfur levels of 67, 338 and 685 ppm, and compared the results to the predictions of the Complex Model [15]. Significance was evaluated at the 90% confidence level. NMHC reductions were substantially larger than predicted by the Complex Model, and NO$_x$ reductions were smaller. Results are shown below:

	Percent Change in Emissions for Sulfur Reduction			
	NMHC		NO$_x$	
	61 → 338 ppm	61 → 685 ppm	61 → 338 ppm	61 → 685 ppm
Testing	+ 6.7	+ 8.9	+ 3.6 (NS)	+ 6.4
CM Prediction	+ 5.2	+ 12.0	+ 10.0	+ 14.7

Takei et al. [16] tested a 1993 TLEV (Transition Low Emissions Vehicle) and a 1994 TLEV with three fuels having sulfur levels of 32, 300 and 500 ppm. The 1994 TLEV was tested with two catalysts systems. One catalyst had Pt/Rh noble metal in both underfloor and close-coupled locations. The second one had a Pd based catalyst in the close-coupled location. When changing fuels from 300 ppm to 30 ppm, emissions did not appear to return to baseline. The authors speculated that the 1994 model year

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vehicle had a leaner calibration than a previously tested 1992 Camry that showed complete reversibility. They also accumulated 10,000 miles on two test fuels – 30 ppm and 500 ppm on the 1993 TLEV. FTP testing was done with the 30 ppm fuel. No preconditioning was carried out except for the normal LA4s used before each FTP. Emissions of NMHC and CO were higher for the catalyst run on 500 ppm, and the difference maintained itself over 4 or 5 FTP tests. There was no difference in NO_x emissions.

In the final AQIRP study, Rutherford et al. [17] reported on testing eight fuels, four of which represented two levels of sulfur, nominally 35 ppm and 320 ppm. Ten 1989 LD vehicles and six Federal Tier 1 vehicles (0.25 g NMHC/mi) were tested. Results are shown below for regulated and toxics emissions. Specific reactivity was calculated and increased as sulfur was reduced, by 2.9% in the 1989 fleet and by 9.3% in the Tier 1 fleet. The results shown here are generally consistent with earlier AQIRP work, and there does not appear to be a major difference between the 1989 fleet and the Tier 1 vehicle fleet, when expressed as percentage differences.

	Percent change in Emissions 320 ppm → 35 ppm Sulfur	
	1989 LDV	Fed. Tier 1 LDV
NMHC	- 13.3	- 18.5
CO	- 9.8	- 16.4
NO_x	- 4.0 (NS)	- 8.9
Benzene	- 17.8	- 24.5
1,3 Butadiene	- 8.5	-12.1
Formaldehyde	+ 27.2	- 5.2 (NS)
Acetaldehyde	+ 2.9 (NS)	- 0.9 (NS)

Sztenderowicz et al. [18] reported on a program carried out by the Petroleum Environmental Research Forum (PERF) on ten 1993/94 vehicles with three fuels having sulfur levels of 25, 300 and 600 ppm. Nine vehicles were certified to California TLEV standards, and one was certified to Federal Tier 1 standards. Results were compared to the 300 ppm fuel and are shown below.

	Percent Change in Emissions 300 ppm → 25 ppm Sulfur		
	HC	CO	NO_x
Ten 1993/94 LDVs	- 24%	- 21%	- 12% (NS)

There appeared to be a non-linear response to sulfur, with a greater impact between 25 ppm and 300 ppm than between 300 ppm and 600 ppm. None of the changes between 300 and 600 was statistically significant, while the NMHC and CO changes between 300 and 25 ppm were statistically significant. The results were compared to those measured in AQIRP, and it was found that the effects measured on a mass basis were somewhat smaller, in part because the overall emissions levels were significantly less. Sulfur effects expressed on a percentage basis were similar or somewhat larger, again probably reflecting the lower overall emission levels.

Takei et al. [19] tested two vehicles with two fuels having sulfur levels of 30 and 300 ppm. One was a 1992 model year California vehicle was certified to Tier 1 standards and was tested at 50,000 miles, and the other was a 1994 model year California vehicle certified to LEV standards and was tested at 100,000 miles. NMHC, CO and NO_x were reduced by 12%, 14% and 18%, respectively for the Tier 1 car, and by 21%, 32% and 25% for the LEV car. No statistical significance levels were reported for these

results. The authors also reported that emission levels did not return to baseline levels after operating on 300 ppm fuel. The effect seemed to be larger for the LEV car, although no statistical analysis was presented.

Schleyer et al. [20] reported on a program carried out by CRC which measured the impact of sulfur in twelve California LD vehicles certified to LEV standards. Four conventional fuels (30 ppm to 630 ppm) and two California fuels (27 ppm and 148 ppm) were tested. A special preconditioning cycle developed in the European Programme for Emissions, Fuels and Engine Technologies (EPEFE) was used to remove any issues of fuel carry-over or irreversibility from the results. Results are shown below for the fleet averages on the conventional fuels at 100,000 miles:

	Change in Emissions 630 ppm → 30 ppm Sulfur		
	NMHC	CO	NO$_x$
grams/mile	- 0.03	- 0.70	- 0.23
Percent	- 32 %	- 46 %	- 61 %

There was a wide range in the responses of individual vehicle models, and those with the lowest emission levels tended to have the smallest response to sulfur. The response to sulfur concentration for the 100,000 mile aged catalysts was non-linear for all three pollutants measured, with a larger response at low sulfur levels. The authors also compared results for similar sulfur ranges across four large test programs that evaluated technologies ranging from Tier 0 to LEV. When the fleet average impacts were expressed in mass terms, the sulfur effect was similar for all fleets, with the possible exception of NO$_x$ in the LEV fleet. However, when expressed as percentages, the effects were larger as base level emissions were reduced with newer technology.

Takei et al. [21] tested four stoichiometric gasoline vehicles (LEV, ULEV, SULEV) on fuels ranging from near zero to 600 ppm, although the ranges were different for each vehicle. In addition, two Japanese direct injection vehicles with NO$_x$ Storage Reduction catalysts were tested For the stoichiometric vehicles, all the vehicles had a response to sulfur, but the SULEV had a the largest response on a relative basis, similar to findings in other programs. The authors found that even at 30 ppm sulfur, the NSR systems had degraded performance in NO$_x$ conversion, NO$_x$ storage capacity and reversibility.

Lyons et al. [22] tested eight 1997/98 model year California vehicles (Tier 1, LEV and ULEV) on two fuels with sulfur levels of 40 and 540 ppm. FTP and US06 driving cycles were used, and special attention was devoted to reversibility and variations in sulfur response between vehicles. The authors concluded that there was a high degree of variability in responses to sulfur, and carried out regression analyses to determine what design factors contributed to the differences. The strong correlations between design factors did not allow them to draw specific conclusions; however, given appropriate resources, experiments could be designed and carried out to develop additional insight into this question.

In 2001, the automotive industry in the U.S. reported on a test program carried out on 13 prototype California TLEVs, LEVs and ULEVs [23]. Three levels of sulfur were tested, 1, 30 and 100 ppm. No details of the statistical analysis were provided, but the results below appear to be statistically significant. Averages quoted in the presentation appear to be geometric averages of the fleet emissions.

	Change in Emissions 100 ppm → 1 ppm Sulfur		
	NMHC	CO	NO$_x$
g/mi	- 0.017	- 0.642	- 0.059
Percent	- 27%	- 42%	- 39%

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Responses are generally linear, although there may be a slight curvature, such that the effect of sulfur is less at extremely low values. The authors postulated that this might be due to the effect of sulfur in the lubricant.

The most recently published study carried out on a relatively large fleet of U.S. vehicles was CRC Project E-60 [24], which tested twelve California vehicles certified to LEV and SULEV standards, and two European vehicles certified to Euro 3 standards. All vehicles were tested with three fuels (5, 30 and 150 ppm sulfur) with as-received and aged catalysts. The objective was to measure ammonia emissions, but regulated emissions were measured as well. All vehicles were tested using the US FTP and US06 cycles; the European vehicles were tested over the NEDC (New European Driving Cycle) as well. For the California vehicles, there was a small but significant effect of higher sulfur on NO_x emissions, and no effect on NMHC and CO emissions. Differences were larger on the US06 cycle, and were statistically significant for NMHC, CO and NO_x. A summary of the results is shown below:

| | Change in Emissions, 150 ppm → 5 ppm Sulfur | | | | |
	NMHC	CO	NO_x	NH_3	N_2O
FTP Test Cycle					
g/mile	-0.001 (NS)	-0.045 (NS)	- 0.022	- 0.003 (NS)	- 0.011
Percent	- 2.2	- 6.4	- 31.0	- 15.8 (NS)	- 64.7
US06 Test Cycle					
g/mile	- 0.025	- 0.569	- 0.102	- 0.020	- 0.010
Percent	- 64.1	- 10.2	- 70.8	- 21.3	- 90.9

In Europe, Morgan et al. [25] carried out a small program on two European cars and sulfur levels between 11 ppm and 116 ppm. They used both the European ECE (Economic Commission for Europe) and the US FTP test cycles, and concluded that reducing sulfur reduced HC, CO and NO_x. No statistical analysis was reported and details of the vehicles were minimal.

The EPEFE program carried out a large study on the sulfur response in European vehicles [26]. Four fuels ranging in sulfur concentration from 18 ppm to 382 ppm were tested in sixteen European vehicles, all fitted with TWC, and either single point or multi-point injection (MPI). Results are summarized below for the combined ECE/EUDC cycle, known collectively as MVEG 2000. The ECE cycle is a cold start urban driving cycle and EUDC is a warmed-up cycle. In the cold start portion, emissions are measured starting from key-on, rather than after a warm-up period as in earlier test cycles. Sulfur effects are generally larger on percentage basis after the catalysts have reached operating temperatures.

| Change in Emissions 382 ppm → 18 ppm Sulfur | | | |
	HC	CO	NO_x
g/km	- 0.015	- 0.113	- 0.019
Percent	- 8.6	- 9.0	- 10.4

The results were generally linear over the range studied, although there was some suggestion of non-linearity for HC and CO emissions. Compared to AQIRP, the relative effects seen in this program are smaller for HC and CO and similar for NO_x.

Some measurements of toxics were made but no statistical analysis could be carried out. Nevertheless, lower sulfur appeared to lower benzene and had no noticeable effect on 1,3 butadiene,

formaldehyde and acetaldehyde. An analysis of vehicle to vehicle differences suggested that palladium based catalysts were more sensitive than platinum/rhodium catalysts. Close coupled catalysts appeared to be more sensitive to sulfur, especially for NO_x, over the EUDC cycle.

Kwon et al. [27] tested a direct injection engine calibrated to meet Euro II emission limits. The vehicle was equipped with a lean NO_x catalyst system. Two sulfur levels (32 and 138 ppm) were tested. No significant differences were seen between the two fuels even at 90% confidence level for HC, CO, NO_x or particulates.

Stradling et al. [28] reported on a CONCAWE study of four advanced gasoline vehicles available in the European market in 2002. Three were direct injection and one had MPI. Two cars met Euro 3 standards and two met Euro 4 standards. Four level of sulfur were tested, covering the range 4 ppm to 148 ppm. The test was designed to see differences of at least 7% for each pollutant measured. All four vehicles showed little or no sensitivity to fuel sulfur. No effects were statistically significant for the entire NEDC driving cycle, but a few responses were statistically significant on the EUDC portion. The HC response was positive for two of four cars the CO response was positive for two cars and negative for one car.

Akimoto et al. [29] studied three sulfur levels (8, 73, 140 ppm) in one Japanese 1993 model year car with MPI and a TWC, using the 10.15 mode emissions test cycle. Reducing sulfur lowered emissions of HC, CO, NO_x and benzene. The reduction in NO_x seemed to be the highest on a relative basis. No statistics were reported, so it is difficult to assess the significance of these results on one vehicle.

Koseki et al. [30] measured sulfur response in six late model Japanese vehicles – three stoichiometric vehicles with TWC, one lean-burn with NO_x storage catalyst, and two direct injection engines with different NO_x reduction catalysts. Each vehicle was tested on fuels varying between 3 ppm and 80 ppm or between 4 ppm and 90 ppm. The 10.15 mode Japanese test cycle was used for all the tests. The authors concluded that the lean-burn engines exhibited a smaller response to sulfur than the stoichiometric engines, although no statistical analysis was presented.

In 2000, Hamasaki et al. [31] presented results of the Japanese Clean Air Program (JCAP), which compared two fuels (96 ppm and 22 ppm) in eleven late model year vehicles intended to approximate the current and future Japanese fleet. Two test cycles were used, the 10.15 mode test and the cold start 11 mode test. The authors found that reducing sulfur lowered emissions of THC, CO and NO_x in both test cycles, although the effect was larger in the hot start 10.15 mode test, when the catalysts were operating a higher fraction of the time. The relative effects appeared to be higher for the low emitting and lean-burn vehicles, because there were fewer pollutants emitted before catalyst light-off. No statistical analyses were presented for the results.

In Phase II of the JCAP program [32], one MPI vehicle with a TWC and three SIDI (Spark Ignition Direct Injection) vehicles with NOx reduction catalysts were tested on sulfur levels of 2, 22 and 86 ppm. The MPI vehicle had a smaller response to sulfur and under some test conditions did not respond at all. The SIDI vehicles had a stronger response, especially on the 10.15 mode test, for NO_x and CO. All vehicles showed a flat response of THC to sulfur changes. The SIDI vehicles exceeded the emission target at the highest sulfur level, but satisfied the target at the lowest level.

Thummadetsak et al. [33] tested six cars representative of the Thai market (model years 1993-96) with fuels having sulfur levels of 50, 100 and 300 ppm. Four cars had TWC, one had an oxidation catalyst and one was a non-catalyst car. For the catalyst equipped vehicles, reducing sulfur from 300 ppm to 50 ppm lowered THC by 7.6% and acetaldehyde by 28%. Changes in CO, NO_x, benzene, 1,3 butadiene and formaldehyde were not significant.

REVERSIBILITY AND AGING

There have been a number of studies, some discussed above, that measured reversibility of the sulfur effect. Most of the earlier studies on sulfur effects found that reversibility was complete and occurred with a short mileage interval.

Bjordal et al. [34] studied the effects of catalyst aging on one 1992 European car with two different catalyst systems. One was aged on gasoline with 50 ppm sulfur and one on fuel with 450 ppm sulfur. Aging was carried out on a test bed using the European EUDC and emissions testing used the European Test Cycle which measures emissions from key on. There was no consistent difference in NMHC emissions between the catalyst aged on low sulfur fuel and the catalysts aged on high sulfur fuel. For CO, aging on high sulfur fuel gave higher emissions at 80,000 km when tested on high sulfur fuel, but not at 40,000 km for either high or low sulfur fuel. NO_x emissions actually increased more when aged on low sulfur fuel, than when aged on high sulfur fuel. Some of the differences were tied to differences in the lambda sensors, although it was not known whether these differences were related to the different sulfur levels or to subtle manufacturing differences. The results of this test, and the difficulty explaining them, show the problems of testing a small number of vehicles and the advantages of larger fleets for this type of work.

Schleyer et al. [35] reported on a CRC program in which two sulfur levels (30 ppm and 630 ppm) were tested over a variety of cycles and the reversibility of the sulfur effect was assessed. Six of the twelve vehicles tested in the CRC Sulfur/LEV program [20] were used. Full reversibility was achieved when emissions returned to the baseline level achieved with 30 ppm fuel after running on 630 ppm fuel. For the entire fleet, NMHC emissions were fully reversible with either the mild LA-4 driving cycle, or the more aggressive US06 driving cycle. CO emissions were fully reversible with the US06 cycle, but only 79% reversible with the LA4 cycle. NO_x emissions were 84% reversible with the LA4 cycle and 95% reversible with the US06 cycle. Where less than full reversibility is shown, the result is statistically significant at the 95% confidence level. In most cases, emissions recovery stabilized within 10 miles of driving.

Lyons et al. [22] tested eight 1997/98 model year California vehicles (Tier 1, LEV and ULEV) on two fuels with sulfur levels of 40 ppm and 540 ppm. FTP and US06 driving cycles were used, and special attention was devoted to reversibility and variations in sulfur response between vehicles. With respect to reversibility, they concluded, "the effects of sulfur were fully reversible, although in some cases, more severe operating conditions such as those encountered in the US06 cycle were required."

REVIEW PAPERS

A number of review papers summarizing and comparing major studies were published in the technical literature. Truex [36] evaluated laboratory and vehicle test programs in an effort to understand the mechanisms of sulfur's impact on emissions in gasoline vehicles. Truex reviewed work on noble metal loadings, base metal interactions and temperature effects. He also reviewed the then published fleet tests. Truex was not particularly sanguine that catalyst systems could be designed without sensitivity to sulfur concentrations, but felt that it might be possible to reduce sulfur sensitivity.

Hochhauser et al. [37] recently published an analysis of sulfur data in fleets with TWC covering seven published studies and one unpublished study. The newest fleets, represented by the CRC E-60 program, and the CONCAWE program on 2003 vehicles, exhibited relatively low responses to sulfur, less sensitive than data from model years 1997 and 1999. The data were analyzed on an absolute basis, and a comparison on a percentage basis would not show the same large differences. Shown below are the responses for NO_x, for the published studies, as presented:

Emission Control Level	Program Sponsor	NO$_x$ Reduction, g/km 150 ppm → 50 ppm
US Tier 0	AQIRP	0.004
US Tier 1	AQIRP	0.006
Euro 2	EPEFE	0.005
California LEV	CRC	0.040
California LEV	AAM/AIAM	0.050
Euro 3/4	CONCAWE	0.001
California LEV	CRC	0.013

In developing the latest version of the ARB Predictive Model, Uihlein also carried out an analysis of previous work, and presented it at a public meeting organized by ARB as part of their effort to update the Predictive Model [38]. The table below compares the relative responses at ultra low sulfur levels from various large programs on late model vehicles included in the ARB database. His analysis showed that at these low levels, results were very similar

Emission Control Level	Program Sponsor	NO$_x$ Reduction, % 20 ppm → 10 ppm
California LEV	CRC	- 3%
California LEV	AAM/AIAM	- 5%
California LEV	AAMA	- 5%
California LEV	CRC	- 6%

PARTICULATES

Particulate emissions as a function of fuel sulfur were studied in a number of programs carried out in Europe. Mohr et al. [39] tested one European gasoline car with two fuels having sulfur levels of <10 ppm and 175 ppm and measured particulate emissions using a number of different instruments and dilution techniques. Emissions were so low with the gasoline vehicle that it was difficult to draw meaningful conclusions. However, the authors measured higher numbers of particles with the higher sulfur fuel measured by the CPC (Condensation Particle Counter) under certain test conditions.

Ntziachristos et al. [40] tested eleven gasoline vehicles (6 MPI and 5 DI) with three fuels having sulfur levels of 6, 45 and 143 ppm. Differences in PM emissions due to fuel sulfur could not be seen because of the low overall emission rates.

It appears that the impact of sulfur on PM emissions from gasoline vehicles, while theoretically possible, is too small to be seen with today's instruments and test protocols.

SULFUR SUMMARY

Reducing sulfur lowers emissions of HC, CO and NO$_x$. Although there is some conflicting data, the effects appear to be linear, especially at levels of sulfur below about 150 ppm. Reducing sulfur also lowers emissions of the air toxics benzene and 1,3 butadiene, and may increase emissions of formaldehyde. The impact on acetaldehyde is less clear. In any case, there is not much recent data on toxics effects.

In 1989 vehicles, the sulfur effect was shown to be totally reversible under mild driving conditions. More recent testing has shown that, in the short term, reversibility is complete only under extreme driving

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conditions. This is likely the result of tight control of engine conditions and temperatures in newer technology, and possibly changes in catalyst formulation.

PM levels are generally low in gasoline vehicles; while sulfur probably has an impact, it is certainly low relative to diesel vehicles, and probably not of regulatory concern.

Research efforts have not been totally successful in developing an understanding of the ways to design emission control systems that are insensitive to sulfur.

Considering the low sulfur levels present in the U.S., Europe and Japan, and the extensive database available on sulfur effects, additional research is not warranted at this time. Changes in gasoline technology, or increased emphasis on particulate emissions from gasoline vehicles, might spur additional research.

B. AROMATICS AND BENZENE

Aromatics compounds are based on six carbon ring structures, the simplest of which is benzene. Higher molecular weight aromatics generally have one or two paraffinic or olefinic sidechains. Aromatics composed of multiple rings, are generically described as multi-ring aromatics, polyaromatic hydrocarbons (PAH) or polynuclear aromatics (PNA). PAHs have high molecular weight and are present in gasoline at low concentrations, if at all. All aromatics have high octane and high energy density. Their boiling points are higher than the average boiling point of other gasoline components.

When considering aromatics, it is important to recognize that the contribution of individual aromatic compounds to emissions performance may differ. Higher molecular weight compounds may have a different impact on emissions than those with lower molecular weight. Sometimes carbon number is used as a surrogate for molecular weight. Benzene, the simplest and lowest molecular weight aromatic, is usually considered separately, because it is a toxic compound and has a strong effect on benzene exhaust and evaporative emissions. The benzene concentration of gasoline is also controlled by regulation.

In the 1980s, average aromatic levels in U.S. gasoline were 32%. There was some evidence that aromatics contributed to high emissions and emissions of benzene. AQIRP carried out a large study to measure the impact of aromatics on exhaust emissions. Hochhauser et al. [41] reported on AQIRP work that measured the effect of aromatic levels between 20% and 45% in twenty 1989 vehicles. (Olefins, MTBE and T_{90} were also studied, and these will be described later.) The effects of this change on fleet average emissions are summarized below:

Percent Change in Emissions 45% Aromatics → 20% Aromatics		
NMHC	CO	NO$_x$
- 11.6-	- 13.3	+ 2.0

All changes shown above were statistically significant (95% CL), NO$_x$ just barely. It was interesting that for engine-out emissions, reducing aromatics reduced NO$_x$, the opposite of the effect seen in tailpipe emissions. Later studies tried to understand this effect which apparently affects the catalysts. Also noted was that the effect on total HC was much smaller that the effect shown above for NMHC. It was shown by Hochhauser et al. [42] that reducing aromatics (and consequently increasing paraffins) contributed to higher methane emissions and lower NMHC emission rates and that reducing aromatics did not impact the specific reactivity of the exhaust (g O$_3$/g HC, MIR scale).

There were a number of interactions with other properties. An interaction with MTBE suggested that lowering aromatics increased NO$_x$ emissions to a greater extent when MTBE was present than when it was absent. Also, an interaction with T_{90} suggested that the heavier molecular weight aromatics were more important than the lower molecular weight aromatics in affecting NMHC and CO emissions.

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Gorse et al. [43] reported result of toxics measurements from the same experiment and the results are shown below:

Percent Change in Emissions 45% Aromatics → 20% Aromatics			
Benzene	1,3 Butadiene	Formaldehyde	Acetaldehyde
- 41.8	+ 11.3	+ 23.5	+ 19.5

The large reduction in exhaust benzene was expected since aromatics can decompose under combustion conditions to produce benzene in the exhaust. No attempt was made to explain the increases in the other toxic emissions in this experiment. The increase in formaldehyde might be related to the increase in exhaust methane seen when aromatics are reduced and are replaced by paraffins, as described below.

Marshall and Gumey [44] evaluated the impact of individual aromatic compounds on exhaust benzene emissions in five 1986 Model Year cars with fifteen fuels and found that fuel benzene had the highest impact on exhaust benzene. Other aromatics tested – toluene, ethyl benzene, xylenes and heavy reformate (C9+) – had an average effect of about 8% of benzene.

API conducted a study on the impact of aromatics as a function of carbon number in ten 1989-90 model year cars [45]. This effectively allowed them to separate the effects of aromatics and volatility. Two sets of fuels were blended. In the first, certain aromatics were removed and replaced by a mix of other aromatics of different carbon numbers to keep the total aromatic level constant. In the second set, certain aromatics were removed and replaced by equivalent iso-paraffins, effectively controlling distillation properties. With the first set of fuels, as the average carbon number of the aromatic compounds became heavier, exhaust emissions of NMHC, CO and NO_x increased. The effect on NO_x was classified as borderline significant ($0.95>p>0.90$). However, when the distillation properties were held constant, shifts in the distribution of aromatic carbon content had no effect on exhaust emissions. This implies that what had been measured as an aromatic effect was really an effect of distillation properties.

Hirota et al. [13] tested two 1991 Nissan Sentras and concluded that reducing aromatics from 33% to 20% reduced NMOG and aromatics in the exhaust, but did not affect specific reactivity.

Takei et al. [16] tested a 1994 Camry TLEV over three aromatics levels, 10%, 29% and 39%. Reducing aromatics lowered CO, especially below about 20% aromatics, but had no effect on HC or NO_x. They did not see the HC effect seen in the AQIRP study, and speculated that lack of effect was because they did not vary heavier aromatics, but adjusted aromatic content by adding toluene. Heavier aromatics (C9+) are thought to have a larger impact on emissions.

Morgan et al. [25] tested 27 cars from Japan, Europe and Canada from model year 1989-91. Eight cars had no catalysts, and the others had TWC systems. Six cars were carbureted, three had throttle body injection and the others had MPI metering systems. Five fuels were tested on all cars, and reducing aromatics seemed to reduce exhaust emissions of HC and CO. However, the authors realized that there was a significant correlation between aromatics concentration and T_{50} levels, so they could not state this conclusion with certainty. No statistical analysis was shown to support the conclusions.

Jeffrey and Elliott [46] tested five European vehicles with 29 fuels, some of which were from the AQIRP study. For the catalysts vehicles tested, they found that aromatics had a significant effect on exhaust emissions. As noted below, reducing aromatics lowered HC and CO and increased NO_x.

Percent Change in Emissions 45% Aromatics → 20% Aromatics		
HC	CO	NO_x
- 10.1	- 12.9	+ 10.6

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These results are very similar to those reported for AQIRP. Similarly, reducing aromatics reduced benzene emissions, but increased emissions of the other toxics, 1,3 Butadiene, formaldehyde and acetaldehyde.

Wedekind et al. [47] studied the effect of aromatics and volatility on emissions in one catalyst equipped European car over the European driving cycle (ECE+EUDC). In eleven fuels, aromatics, T_{50} and T_{90} were varied independently. As in other programs, reducing aromatics lowered HC and CO and increased NO_x emissions. Emissions of toxics were also measured. Reducing aromatics lowered benzene emissions and raised emissions of 1,3 butadiene. The authors attribute the latter effect to an increase in paraffins that occurs when aromatics are lowered.

The EPEFE program studied aromatics and mid-fill volatility in sixteen European vehicles with nine fuels [48]. The vehicles were prototypes intending to meet the 1996 emissions limits. The year 2000 driving cycle (ECE+EUDC) was used. A full regression analysis revealed that reducing aromatics lowered HC and CO but increased NO_x emissions. There were significant interactions between aromatics and E100 for HC and NO_x. These results are fully consistent with other programs and also showed, as in previous studies, that reducing aromatics lowered engine-out NO_x. NO_x catalyst efficiency dropped for the low aromatic fuel and tailpipe NO_x emissions increased. Reducing aromatics lowered benzene emissions, but increased emissions of 1,3 butadiene, and aldehydes.

E100 Level (Mid-Fill Volatility)	Percent change in Emissions 50% Aromatics→ 20% Aromatics		
	HC	CO	NO_x
35	-31.7	- 16.8	- 15.0
50	- 10.9	- 18.5	- 8.3
65	- 10.2	- 17.4	- 2.7

Bennett et al. [49] tested three Euro 1 and three Euro 2 vehicles with a number of fuels, including two matched fuels having aromatics levels of 41.5% and 27.5%. In contrast to results from other programs, they did not see an impact on HC or NO_x, and CO emissions increased when aromatics were reduced. McDonald et al. [50] tested 7 fuels in 12 TWC equipped European vehicles (1990-93 model year) and did see the expected results; i.e. reducing aromatics lowered emissions of HC and CO and increased NO_x emissions.

CONCAWE analyzed data from European companies and an Italian industry program on the relationship between benzene and aromatics in the fuel and exhaust benzene emissions [51]. Emissions data from 21 non-catalyst cars and 34 catalyst cars were used. Data showed that fuel benzene had the largest influence on exhaust benzene and that the impact of NBA (non-benzene aromatics) was about 90% less. A comparison to the EPA Simple and Complex Models was developed as shown below. The ratios are similar and the authors concluded that similar mechanisms are at work in all tests.

Relative Contribution of Benzene/NBA to Exhaust Benzene Emissions		
CONCAWE (Catalyst cars)	EPA Simple Model	EPA Complex Model
Percent Benzene	7.8	8.4	
Mass Benzene	10.0		8.4 *
* Based on normal emitters and total aromatics, not NBA		

The question of the aromatic effect on NO_x emissions was investigated by Le Jeune et al. [52] in two European vehicles with six full boiling range fuels and 23 fuels blended from individual chemicals such as toluene and iso-octane. The vehicles were tested over the European emissions cycle consisting of the ECE15 and EUDC driving cycles. Both vehicles exhibited an increase in engine-out NO_x emissions when aromatics increased. This effect is consistent with the higher energy content and higher flame temperatures of aromatic compounds versus paraffinic compounds. Both vehicles also exhibited an increase in catalyst efficiency for NO_x reduction when aromatics increased, presumably due to the higher concentration of aromatics in the exhaust. In one vehicle, which had relatively loose control of A/F (Air/Fuel) ratio, the increased efficiency was smaller and did not overcome the higher engine-out emissions. The other vehicle had tight control of A/F ratio, a bigger increase in catalyst efficiency, and consequently lower tailpipe NO_x emissions. These data and conclusions explain the results seen in AQIRP and other studies.

Van den Brink and McDonald [53] demonstrated in a laboratory reactor that aromatics in the exhaust stream contribute to enhanced NO_x reduction. Methane and ethane, produced in larger quantities with low aromatic/high paraffin fuels, were very unreactive. There were also indications that aromatic fuels caused a slight shift in the A/F ratio toward rich mixture. Replacing aromatics with paraffins or olefins would increase methane in the exhaust gas which would reduce catalytic NO_x activity, and would shift the stoichiometry toward the lean side, which would also tend to reduce NO_x efficiency.

Graupner et al. [54] investigated the NO_x/aromatics effect in a bench engine at steady state and in a TWC equipped vehicle with a number of carefully blended fuels. Detailed studies showed that reducing aromatics in the gasoline increased the amount of hydrogen in the exhaust, and the presence of higher levels of hydrogen changed the response of the lambda sensor, causing the engine to shift to a slightly leaner stoichiometry. This occurred only when the engine, catalyst and sensors were warmed-up, showing that the sensitivity of a vehicle to aromatics levels depends on the calibration of the vehicle. The authors also reasoned that using a lambda sensor in a post-catalyst position, where there is little if any hydrogen, would mitigate this effect. They activated the feedback control of A/F ratio by using the rear oxygen sensor found on OBDII systems, and found that the aromatics/NO_x effect was virtually eliminated.

The Japanese Clean Air Program (JCAP) studied two levels of aromatics (37% and 22%) in a fleet of nineteen vehicles, targeting advanced and future technologies [31]. Among the vehicles were two lean-burn GDI vehicles and two lean-burn port injection vehicles. Two test cycles were used, the 10.15 mode and the 11 mode. It was reported that reducing aromatics lowered HC and CO emissions and increased NO_x emissions in the 10.15 mode test. In the 11 mode test, reducing aromatics had a different impact reducing THC and NO_x, and increasing CO. No statistics were provided, and there was no discussion about why the responses were different for the two test cycles.

Most of the test work on aromatics in the past ten years has focused on direct injection gasoline engines. Since these have been more common outside the U.S., most of the published data has come from Japan and Europe. Direct injection gasoline engines can operate in a stoichiometric mode or in a lean mode. In stoichiometric mode, fuel responses might be similar to port injected engines. In lean mode, fuel responses are less predictable, since the combustion regimes are different. Also, in lean

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mode, control of NO_x emissions is similar to diesel engines and if catalytic control of NO_x is required, the standard TWC would not be appropriate.

Kwon et al. [27] studied one lean-burn GDI car, calibrated to meet Euro 2 standards, using the Euro 2 test cycle. Two aromatic levels were compared, 40% and 25%, and no statistically significant differences were seen in HC, CO, NO_x or PM emissions.

Stradling et al. [28] tested three GDI cars (two lean-burn and one stoichiometric) complying with Euro 3 and Euro 4 emission limits. Emissions control systems for the lean-burn engines consisted of TWC and NO_x traps. Aromatic levels varied between 26% and 38% in a half-factorial design. Results were reported for each of the cars individually, probably because of the significant technology differences. Reducing aromatics reduced HC emissions in both lean-burn cars, but not in the stoichiometric GDI car. Reducing aromatics also reduced NO_x in one of the lean GDI cars and had no effect in the others. The test design had good statistical power and would most probably have detected a difference in emissions of 7% or greater.

In the second phase of JCAP [32], three aromatics levels (8%, 30% and 50%) were tested in three lean-burn GDI cars and one port injected stoichiometric car. The impact of reduced aromatics was not consistent among the cars, and was not consistent with results reported in the literature for port injected vehicles. The authors speculated that the responses were determined by details of the engine map that controls how injection timing and duration is impacted by changes in fuel density.

Sogawa et al. [55] measured PM emissions at two levels of aromatics (46% and 40%) in a lean-burn GDI 1993 model year Japanese car. No differences were reported, possibly because of the relatively close aromatic levels, and possibly because the PM levels were so low that the test and measurement variances were too high to see differences.

Hirose et al. [56] tested one 2005 model year Japanese lean-burn GDI car in 9 different gasolines, primarily to test the impact of oxygenates on PM emissions. However, aromatics also varied somewhat and a regression analysis showed that aromatics were a large contributor to PM number emissions in both the 10.15 mode test cycle and the 11 mode test cycle.

Thummadetsak et al. [33] tested six vehicles (1993-96 model year) representative of the fleet in Thailand. Four had TWC, one had an oxidation catalyst and one was a non-catalyst carbureted vehicle. Three levels of aromatics were tested – 20%, 35% and 45%. Results for the catalyst vehicles are shown below:

Percent change in Emissions, 45% Aromatics → 20 % aromatics						
HC	CO	NO_x	Benzene	1,3 Butadiene	Formaldehyde	Acetaldehyde
-7.5	- 5.96 (NS)	- 14.2	- 36.3	+ 1.3 (NS)	+ 12.6 (NS)	+ 19.5 (NS)

Consistent with other programs, reducing aromatics lowered HC emissions. However, NO_x emissions were reduced also, by an amount more in line with engine-out emissions. It is possible that the:

- factors described by other researchers for increasing NO_x at lower aromatic levels may not be present in the Thai marketplace,
- vehicles are calibrated for a higher aromatics level,
- lambda sensors are not as sensitive to the aromatic and hydrogen content of the exhaust, and
- control of stoichiometry is not as tight as it is on some of the vehicles tested in other programs.

A number of studies have examined fuel effects in European 2-wheelers such as motorcycles and mopeds. Prati et al. [57] measured emissions from sixteen in-use mopeds and six motorcycles over two driving cycles, ECE 47 and ECE 40. In both cycles, emissions are sampled after engine warm-up. All the

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vehicles had 2-stroke engines and none had catalytic aftertreatment devices. Two fuels were used, differing primarily in benzene (1% and 0.7%) and aromatics (28% and 33%), although E100 was also different (48% and 58%). The authors concluded that the lower benzene/lower aromatic fuel had lower benzene emissions, and that HC, CO and NO_x emissions were unaffected by fuel quality. No statistical analysis was presented.

Jain et al. [58] tested twelve 2-wheelers on three gasolines varying in aromatics (10% to 62%) olefins (1% to 26%) and benzene (0.3% to 1.5%). Benzene and aromatics levels were correlated. The 2-wheelers were 2000-2004 model year Indian vehicles, both new and in-use. Three had 4-stroke engines and three were 2-stroke. HC, CO and NO_x emissions were not affected by aromatics. Benzene emissions were measured and were much higher for the high benzene/high aromatics fuel.

SUMMARY OF AROMATICS AND BENZENE EFFECTS

In most studies carried out to date, reducing aromatics lowered emissions of HC, benzene and CO. A number of studies suggest that heavier aromatics (C9+) contribute to increased HC/CO emissions more than lighter aromatics (C7, C8), although a well designed API study concluded that the effect was due to molecular weight and volatility.

There is good evidence that reducing aromatics lowers engine-out NO_x emissions but also lowers the efficiency of TWC systems. The net effect is usually an increase in tailpipe NO_x emissions, and probably depends on the design of the specific engine control and aftertreatment systems.

Benzene and non-benzene aromatics contribute to exhaust benzene emissions. The contribution of non-benzene aromatics to exhaust benzene emissions is about 1/10 the contribution of benzene.

C. OLEFINS

Olefins are a class of HC compounds that contain one or more unsaturated or double carbon-carbon molecular bonds. The presence of these double bonds makes olefins reactive in the combustion process, easy to oxidize over a catalyst, but also highly efficient in forming atmospheric ozone. Although light olefins are produced in the combustion process, fuel olefins are present only with molecules having five or more carbon atoms. Olefins in the exhaust are major contributors to the total exhaust ozone reactivity.

AQIRP [41-43] studied the impact of olefin levels on exhaust emissions in 20 1989 model year vehicles as part of a larger study evaluating a number of fuel variables. The effect of reducing olefins from 20% to 5% on exhaust emissions is shown below:

	Percent Change in Emissions 20% Olefins → 5% Olefins
NMHC	+ 7.1
CO	+ 1.5 (NS)
NO_x	- 6.1
Specific Reactivity	- 8.0
Benzene	- 3.0 (NS)
1,3 Butadiene	- 31.6
Formaldehyde	+ 1.3 (NS)
Acetaldehyde	-3.7 (NS)

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Olefins are more reactive in the combustion process, and reducing olefins and replacing them with paraffins results in a mixture that will not burn as completely or as fast, thereby causing increases in HC emissions. Furthermore, the engine-out exhaust, since it contains lower olefins levels, will also be less reactive over the catalyst. Engine-out emissions followed the same trend as tailpipe emissions, supporting this theory. On the other hand, less complete combustion results in lower heat release and therefore lower NO_x emissions. CO emissions are generally formed when the mixture is rich, and therefore not affected by changes in olefin concentration, which do not affect stoichiometry.

Olefins in the fuel were highly correlated with olefins in the exhaust. Since olefins are highly reactive in terms of ozone formation, it follows that the specific reactivity of the exhaust is also reduced when olefin levels are reduced.

The only significant impact of olefins on toxics emissions was to reduce emissions of 1,3 butadiene. This is not surprising, considering the high correlation between fuel olefins and exhaust olefins.

In the AQIRP study of high emitters [10], the effects of olefins were almost the same as they were on normal emitters. This suggests that the effects are due to the combustion process and not heavily dependent on catalyst efficiency or stoichiometry.

Jessup et al. [59] purported to study olefins, but found effects that were exactly opposite to the AQIRP results. Unfortunately, in the fuel set used by Jessup et al., the olefin and sulfur concentrations were hopelessly confounded, making it impossible to separate the two. Interestingly, Jessup et al. also claimed that there was no sulfur effect.

As part of a larger program, Morgan et al. [25] tested 19 catalyst vehicles from Europe, Japan and U.S. on two fuels having olefin levels of 5% and 15%. They concluded that the data suggested that lowering olefins would increase HC and reduce NO_x emissions. No statistical analysis was presented.

Mayotte et al. [14] tested 39 1986-1990 model year LD in-use vehicles with 12 fuels. Twenty-one of the vehicles were normal emitters and 12 were high emitters. The authors concluded that the low olefins fuel had lower emissions of NO_x and CO, with no impact on HC. The authors recognized that the variables were not totally separated and the low olefins fuel also had a very low T_{50} value.

In Europe, Jeffrey and Elliott[46] tested five European vehicles with 29 fuels, some of which were from the AQIRP study. For the catalysts vehicles tested, results were very similar to those found in AQIRP, as shown below:

Percent Change in Emissions 20% Olefins → 5% Olefins		
HC	CO	NO_x
- 10.8	Unchanged	+ 16.5

Bennett et al. [49] tested three Euro 1 cars and three Euro 2 cars with seven fuels, two of which had different olefin levels (3.9% and 13%). They concluded that reducing olefins reduced emissions of 1,3 butadiene by about 20%, and in the Euro 1 cars, NO_x emissions as well.

In a test of one GDI vehicle with a lean NO_x catalyst, Kwon et al. [27] found no impact of olefin concentration, comparing two fuels having olefin content of 4% and 15%.

Stradling et al. [28] tested four Euro3/4 cars, three of which were GDI and one which was MPI. Olefin levels varied between 3% and 14% in an eight fuel half-factorial design. An olefin effect was seen in only the MPI vehicle, where reducing olefins reduced CO emissions. Differences of more than 7% would have been statistically significant.

Pentikainen et al. [60] tested four European vehicles, five Japanese vehicles and one US vehicle from model years 1999-2003. Two levels of olefins were tested, 4% and 14%. The high olefin levels were achieved by replacing alkylate with iso-octene. This evaluated the question of whether olefin effects

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are caused by heavy olefins. They concluded that increasing the concentration of heavy olefins did not affect any of the regulated emissions (HC, CO, NO_x), ozone forming potential of the emissions, emissions of toxic compounds or PM. The only difference measured was an increase in emissions of iso-butene when heavy olefins increased. This was probably a product of iso-octene partial combustion.

Thummadetsak et al. [33] studied two olefin levels (5%, 10%) in six 1993-96 model year vehicles representative of the vehicle population in Thailand. One vehicle had no catalyst, one had an oxidation catalyst and four had TWC systems. In the catalyst vehicles, reducing olefins reduced THC emissions by 2.5% and benzene emissions by 8.6%. There were no statistically significant olefin effects in the non-catalyst vehicle.

Jain et al. [58] tested twelve 2-wheelers on three gasolines varying in aromatics (10% to 62%) olefins (1% to 26%) and benzene (0.3% to 1.5%). The fuel variables were not independent because they were testing typical refinery fuels. The 2-wheelers were 2000-2004 model year Indian vehicles, both new and in-use. Three had 4-stroke engines and three were 2-stroke. CO emissions were higher for the high olefin fuel and NO_x was not affected. No statistical analysis was provided to support these conclusions.

SUMMARY OF OLEFIN EFFECTS

The impact of olefins has been consistent in the literature. Reducing olefins increases emissions of HC and 1,3 butadiene, and lowers emissions of NO_x. Exhaust specific reactivity is also lowered when olefins are reduced. It is fairly certain that the overall reactivity of olefins contributes to these effects.

D. VAPOR PRESSURE

Front-end volatility of gasoline is usually characterized by two measures – vapor pressure and T_{10}, the temperature at which 10% of the gasoline evaporated in a laboratory batch distillation (ASTM method D 86). Vapor pressure is usually expressed as Reid Vapor Pressure (RVP), which measures vapor pressure of the gasoline sample at a fixed vapor-liquid ratio. The original test measured the pressure in a bomb, but current versions such as ASTM D5191 use more sophisticated and automated equipment that has much better repeatability and reproducibility.

RVP and T_{10} are highly correlated, and only one program [59], discussed below, attempted to separate the two variables. In most of the literature, RVP was the controlled variable, and analysis was carried out in terms of RVP, not T_{10}. For HC fuels, RVP can be easily varied by changing butane concentration in the fuel.

The RVP requirement of vehicles varies as a function of temperature. RVP that is too low will result in poor starting and cold drivability. RVP that is too high will result in vapor-lock and poor hot drivability. ASTM D 439 provides guidance on the appropriate level for RVP as a function of location and month.

RVP is also controlled to limit evaporative emissions. Even though all U.S. LD vehicles are equipped with carbon canisters to trap evaporative HC emissions, RVP can still impact these emissions.

Another aspect of RVP is that the addition of ethanol to gasoline increases the RVP by as much as 1 psi. This increase is a result of the non-ideal, non-linear blending characteristics of ethanol due to hydrogen bonding in the fuel. Other alcohols exhibit the same impact to a greater (methanol) or lesser extent (propanol, butanol). For this reason, many of the programs that measured the impact of RVP on exhaust emissions, also tested ethanol and other oxygenates. The impact of ethanol and other oxygenates will be discussed below.

Most [61] reported on a CRC program that tested twelve TWC vehicles with eight fuels at three temperatures and two altitudes. Although the program was aimed primarily at evaluating oxygenate effects, two different RVP base fuels were tested. The data suggested that reducing RVP from 13 psi to

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11.5 psi might reduce CO at 35°F (2°C) and 50°F (10°C), but Most concluded that more work would be needed to fully define the effects.

AQIRP tested the effects of RVP, ethanol, MTBE and ETBE in twenty 1989 model year vehicles with 11 fuels. RVP varied between 8 and 10 psi [62]. A summary of the effects is shown below:

	Percent Change in Emissions, Reduce RVP 1 psi in the presence of			
	No Oxygen	Ethanol	MTBE	Average Effect of RVP
NMHC	-4.0 (NS)	**- 11.2**	- 1.0 (NS)	**- 4.3**
CO	**-10.4**	- 14.9 (NS)	- 2.4 (NS)	**- 9.1**
NO$_x$	+ 1.5 (NS)	+ 0.4 (NS)	- 6.2 (NS)	- 0.7 (NS)
Benzene	- 0.4 (NS)	+ 0.1 (NS)	- 8.1 (NS)	- 2.4 (NS)
1,3 Butadiene	+ 2.8 (NS)	+ 1.9 (NS)	- 0.4 (NS)	+ 1.8 (NS)
Formaldehyde	- 15.6 (NS)	+ 61.3 (NS)	+ 48.4 (NS)	+ 6.8 (NS)
Acetaldehyde	- 12.8 (NS)	+ 20.5 (NS)	+ 537 (NS)	- 3.3 (NS)

The effects of reducing RVP were statistically similar for the three base fuels, and an average was calculated. Reducing RVP was estimated to reduce emissions of NMHC and CO, but did not change NO$_x$ emissions. The variability of the data for some of the toxics measurements was substantial and even large differences were not statistically significant. The effect of RVP on specific reactivity was small and not statistically significant.

AQIRP also studied RVP changes in seven high emitters. Knepper et al. [10] found there was no discernible effect of RVP on any exhaust emissions in the fleet of seven vehicles.

Jessup et al. [59] claim to have found an effect of RVP on NO$_x$ emissions, such that lowering RVP lowers NO$_x$. Unfortunately, in the fuel set, T_{10} and RVP were hopelessly confounded and the regression analysis found that a T_{10} effect that was exactly opposite the RVP effect, effectively canceling it out. This is a common statistical error, and no conclusions about the impact of RVP can be drawn from this study.

Korotney et al. [63] tested 19 LD vehicles (1986-1990 model year) with eight fuels. A subset of the fuels had good separation of RVP. The vehicles were split between eleven normal emitters and eight high emitters. Although they did not directly compare the two RVP levels, it appears that there was no impact of changing RVP on any of the exhaust emissions.

Rutherford et al. [64] reported on a test carried out in Los Angeles and Las Vegas, with 30 in-use cars in each location. Two RVP levels were tested (9 psi and 12 psi) under typical wintertime conditions [40°F-65°F (4°C-18°C) for Las Vegas and 50°F-70°F (10°C-21°C) for Los Angeles]. The Los Angeles base fuel contained 11% MTBE and the Las Vegas base fuel contained 10% ethanol. The authors concluded that reducing RVP from 12 psi to 9 psi resulted in 12% reduction in CO emissions under Las Vegas test conditions. No significant differences were seen for the Los Angeles tests. Further analysis by Hoekman et al. [65] suggested that the lack of effect in Los Angeles might have reflected a poor state of repair of some of the vehicles.

Bennett et al. [66] tested five 1992-94 model year European cars with six fuels varying in RVP and E70, and with two levels of MTBE, 0 and 10%, using the new European test cycle (sampling from key on). In non-oxygenated fuels, reducing RVP from 1040 bar to 630 bar (15.1 psi to 9.1 psi) reduced CO by 13% and NO$_x$ by 15% and had no effect on HC. The effects were non-linear, with smaller changes in CO and NO$_x$ as RVP was lowered. In the presence of MTBE, reducing RVP lowered NO$_x$ by 10%, but did not affect HC or CO. The effect of RVP on CO was related to the canister purge strategy. Lower RVP fuels

gave less enrichment during canister purge periods, probably because they generate less vapor and do not affect stoichiometry as much.

Thummadetsak et al. [33] tested three RVP levels (45 kPa, 55 kPa, and 62 kPa) in six cars representative of the vehicle population in Thailand. Changes in RVP did not have a statistically significant effect on any exhaust emissions.

SUMMARY OF RVP EFFECTS

There is limited data on the effect of RVP on exhaust emissions. The most consistent data seems to be from the AQIRP study which concluded that reducing RVP would lower exhaust emissions of HC and CO. More recent data have been somewhat variable. Since the most important reason to reduce RVP is to lower evaporative emissions, and since most gasoline RVP is fairly low, it might be worthwhile to collect data on recent model year vehicles to understand the impacts of RVP on exhaust emissions at low levels of RVP. There is also limited data available at low temperatures on the RVP effects. If this is relevant from a regulatory perspective, then additional data would be useful.

E. MID-FILL AND BACK-END VOLATILITY

Gasoline volatility is usually described by the ASTM D86 distillation test discussed earlier. Results of the distillation are plotted on a chart with temperature on the y-axis and percent evaporated on the x-axis. Distillation parameters may be described by "T-numbers" or "E-numbers." T_{xx} refers to the temperature at which a certain fraction of the fuel has evaporated in the distillation. Exx refers to the percent of the gasoline sample that has evaporated at a given temperature. Both measures are equivalent and emissions data may be correlated with either measure. EPA used E-numbers in the Complex Model and ARB used T-numbers in the Predictive Model. Gasoline blenders generally prefer to use E-numbers since they behave in a linear fashion when mixing different refinery blendstocks.

Due to the nature of gasoline blending, there is generally a high degree of correlation between distillation values that are close to each other: e.g., T_{50} and T_{60} or E70 and E80. When distillation measures are far away, say T_{10} and T_{90}, then there is probably not much correlation between them among groups of fuels.

Usually, three measures of gasoline volatility are used in order to get good separation of variables – front-end, mid-fill and back-end volatility. Front-end volatility, discussed above, is usually expressed as T_{10}. Mid-fill volatility is usually expressed as T_{50}, which is basically the median distillation temperature. Back-end volatility is usually expressed as T_{90}. Expressed as E-numbers, these parameters are usually E100, E200, and E300 (in degrees F). In typically refinery blends, there is a high degree of correlation between mid-fill and back-end volatility. When carrying out experimental programs, a great deal of care must be spent on choosing blendstocks to be able to determine the independent effects of mid-fill and back-end. This was achieved with greater or lesser success in the programs described below. In some cases, the authors recognized the lack of orthogonality, while in others it was ignored, calling the conclusions into question.

Another function stated in terms of volatility is the Drivability Index (DI). First proposed in the early 1980s, it has the form:

$$DI = 1.5 \times T_{10} + 3 \times T_{50} + T_{90}$$

It was found that this equation correlates well with start-up and warm-up driving performance of the automotive fleet. The DI equation has been incorporated into gasoline certification standards such as ASTM D 4814. Some have suggested that the DI equation should also be used to correlate exhaust emissions. As will be shown below, both from a fundamental perspective and from a statistical perspective, this is an unrealistic goal.

Recently, it has been found that ethanol and other oxygenates do not act like HC in terms of their effects on drivability and the driveability equations has been modified to:

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$$DI = 1.5 \times T_{10} + 3 \times T_{50} + T_{90} + 20 \times \%oxygen$$

Not much work was done before AQIRP on exhaust emissions and volatility. Clarke [67] had done work in the early 1970s, showing the effect of volatility on emissions. Much of the impact was believed due to measurable performance debits. Cars that stall or hesitate will certainly have higher emissions because of those malfunctions. In the late 1980s, it was realized that emissions might be impacted even when performance debits such as driveability demerits could not be measured.

Gething [68] correlated emissions with DI and found that HC emissions increased when DI increased. However, he did not attempt to determine the best coefficients for the relationship.

One of the main objectives of AQIRP was to determine the impact of volatility parameters on emissions. In the first published AQIRP study, Hochhauser et al. [41] reported on an experiment which varied T_{90} between two relatively extreme values in 20 1989 model year LD vehicles. Results are shown below, along with toxics results reported elsewhere [42, 43]. Lowering T_{90} reduced NMHC exhaust emissions by 23%, and specific reactivity and toxic emissions by similar amounts. This was the largest effect measured in the program. There were a number of higher order interactions, some suggesting that heavy aromatics were more significant than heavy paraffins or olefins in contributing to NMHC emissions. It was speculated that T_{90} affected emissions, especially during cold start operations, because the heavy molecules represented by the back-end of the distillation curve are harder to vaporize and burn before the engine has reached full operating temperature.

	Percent Change in Emissions T_{90}: 360°F (138°C) → 280°F (182°C)
NMHC	- 22.9
CO	+ 1.2 (NS)
NO$_x$	+ 4.9
Specific Reactivity	- 18.0
Benzene	- 10.8
1,3 Butadiene	- 36.8
Formaldehyde	- 25.7
Acetaldehyde	- 23.9

In AQIRP tests of high emitters [10], reducing T_{90} had little or no effect on NMHC and CO emissions, but lowered NO$_x$ emissions significantly. No attempt was made to explain the differences between the normal and high emitter results.

The AQIRP authors also recognized that T_{90} and T_{50} were correlated in the fuel set, and that the results could be explained almost as well by considering T_{50} as the important variable in the regression equations, or by using both T_{50} and T_{90}. The correct interpretation of the results would be that reducing both mid-fill and back-end volatility together could help to reduce NMHC emissions. Programs carried later in the AQIRP, which studied this effect in more detail and attempted to separate the two variables, are discussed below.

In a follow-up AQIRP program, Koehl et al. [69] reported on tests carried out in ten 1989 model year vehicles. In Matrix A, various refinery streams or portions of the streams were added to a base blend. The components varied in carbon number, aromatic and olefin concentrations, and were prepared from fluid catalytically cracked and reformate streams. In Matrix B, heavy paraffins and heavy aromatics were compared directly, and levels of T_{50}/T_{90} were varied independently. The latter was accomplished by changing isomerate and light alkylate concentrations. The authors concluded that:

- The response of NMHC to changes in T_{90} was non-linear, with larger emissions increases occurring as heavier components were added. The effects occurred primarily in Bag 1 of the FTP test.

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- The effects can be attributed to distillation characteristics, not chemical composition differences between aromatics and paraffins.
- Increasing T_{50} levels increased NMHC emissions. The effect did not appear to be non-linear, and was smaller than the T_{90} effect, especially at levels of T_{90} above 315°F (157°C).
- Expressing distillation parameters as percent evaporated variables (E-numbers) provided a better correlation of NMHC than expressing them as distillation temperature variables (T- numbers).
- Fuel composition (i.e., aromatics and paraffin levels) were the most useful predictors of toxics emissions and ozone reactivity effects.

AQIRP tested three vehicles fleets in a more targeted program to measure the independent impacts of T_{50} and T_{90}, reported by Rutherford et al. [17]. Ten 1989 model year vehicles, six 1994 model year Tier 1 vehicles, and six advanced technology vehicles were tested. The advanced technology vehicles had NMHC emission levels below 0.1 g/mi. Results for the fleets are shown below:

	Percent Change in Emissions		
	1989 Model Year	1994 Model Year	Advanced Technology
T_{50} (215°F → 185°F; 102°C → 85°C)			
NMHC	- 5.8	- 4.0 (NS)	- 11.5
CO	- 5.1 (NS)	- 6.9 (NS)	- 5.6
NOx	+ 7.8	- 0.6 (NS)	+ 6.0 (NS)
Benzene	- 3.9 (NS)	- 4.1 (NS)	- 10.8
1,3 Butadiene	- 3.9 (NS)	- 4.2 (NS)	- 11.5
Formaldehyde	+ 2.6 (NS)	+ 0.8 (NS)	- 5.2 (NS)
Acetaldehyde	+ 1.5 (NS)	- 1.5 (NS)	- 10.3 (NS)
Specific Reactivity	- 1.4	- 3.0 (NS)	- 0.8 (NS)
T_{90} (325°F → 280°F; 163°C → 138°C)			
NMHC	- 7.3	- 8.0	- 10.4
CO	+ 10.7	+ 6.6 (NS)	+ 17.2
NOx	+ 1.2 (NS)	+ 11.0	+ 3.7 (NS)
Benzene	- 1.8 (NS)	- 9.7	+ 0.7 (NS)
1,3 Butadiene	- 19.2	- 22.7	- 17.1
Formaldehyde	- 11.9	- 15.1	- 17.0
Acetaldehyde	- 11.3	- 15.1	- 4.6 (NS)
Specific Reactivity	- 11.5	- 8.8	- 4.9

Both T_{50} and T_{90} reduced NMHC exhaust emissions by similar amounts for the three fleets. Since only two levels were tested, it was not possible to evaluate the non-linearity of the effects. NO_x effects were generally small and not significant. Lowering T_{50} seemed to reduce CO, while lowering T_{90} seemed to raise CO; the effects were similar across fleets, although they were not always statistically significant. Lowering T_{50} and T_{90} generally reduced exhaust emissions of toxics, although the T_{90} impact was larger and more likely to be statistically significant.

Kanehara et al [70] tested four 1990 model year vehicles with fuels having three levels of T_{50} (87°C, 96°C, 110°C) using the US FTP emissions test. They concluded that lowering T_{50} reduced exhaust HC emissions, increased NO_x emissions and did not impact CO emissions. No statistical analysis was presented and no quantitative analyses were shown.

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In a program carried out in vehicles similar to those tested in AQIRP, Jessup et al. [59] found that T_{50} had a large effect on HC emissions, and that both T_{50} and T_{90} had large effects on CO emissions.

Takei et al. [11] reported on two vehicles certified to emission level of 0.25 g NMHC/mi. Reponses to T_{90} were very similar to those found in AQIRP. They did not find a strong correlation between T_{50} and NMHC emissions. In a subsequent study [16] Takei et al. tested a 1994 model year TLEV with fuels that independently varied T_{50} and T_{90}. Lowering T_{50} from 105°C to 85°C reduced HC emissions, but the effect was not a strong one and CO and NO_x emissions were not significantly affected. Lowering T_{90} from 161°C to 135°C also reduced HC emissions, and reducing T_{90} further achieved no further reduction in emissions. Reducing T_{90} also increased NO_x emissions by as much as 40%. These results are similar to those found in AQIRP, although the magnitude of the NO_x effect is very large. It should be recognized that this study only tested 1 car, so the results may not be representative of an entire fleet.

Takei et al. [19] tested two vehicles - model years 1992 and 1994 – on eight fuels where T_{50} and T_{90} were varied independently. The non-linear responses of NMHC to T_{50} and T_{90} were similar to that found in other studies. At low levels of each ($T_{50}<90$°C, and $T_{90}<135$°C), NMHC emissions tended to rise. The T_{50} effect was ascribed to the impact of mid-fill volatility on driveability, and the T_{90} effect was ascribed to adsorption and desorption of HC in the oil film present in the combustion chamber. The impact of T_{50} and T_{90} on CO was similar to its effect on NMHC. T_{50} had little effect on NO_x, and T_{90} had an inconsistent effect for the two cars.

Takei et al. [21] tested one LEV and one ULEV on 15 fuels varying in T_{50}, T_{90}, aromatics, olefins, RVP, and oxygenate content. Results are shown for the impact of midfill (T_{50} or E100) and Driveability Index only. Above a T_{50} value of about 100°C, exhaust HC emissions rise sharply, about 40% or 60% in 20°C. Below this level, emissions are flat. NO_x shows the opposite effect. Below a T_{50} level of 100°C, emissions rise by 30% and 50% as T_{50} is reduced 20°C.

The most recent program to study mid-fill and back-end volatility was CRC Project E-67 [71] in which 12 California certified vehicles were tested with 12 fuels varying in T_{50}, T_{90} and ethanol. Three levels of each variable were tested in a fractional factorial design that allowed second order interactions to be evaluated. The vehicles were 2001-2003 model years and had certification levels of LEV, ULEV and SULEV. Fuels properties spanned the 10th and 90th percentiles for T_{50} and T_{90} based on U.S. summertime surveys. In addition, two levels of T_{50} were evaluated for speciation and toxics emissions.

The effects of T_{50} and T_{90} on NMHC emissions were non-linear, similar to the response seen in earlier studies. At low levels, the response was lower than at high levels. Fleet average increase in emissions of NMHC were 36% and 25% in going from the low T_{50} (195°F, 91°C) and midpoint T_{50} (215°F, 102°C) to the high T_{50} (235°F, 113°C). The T_{90} response depended on the ethanol concentration in the blend. When no ethanol was present, changing T_{90} did not affect NMHC emissions. At 5.7% and 10% ethanol, the effect was non-linear, with a smaller effect going from low T_{90} (295°F, 46°C) to mid T_{90} (330°F 166°C) than going from mid T_{90} to high T_{90} (355°F, 179°C). Effects of T_{50} and T_{90} on CO emissions were somewhat mixed. The T_{50} response appeared to be non-linear for fuels that contained ethanol, but was essentially flat for the non-ethanol fuels. CO emissions decreased as T_{90} increased. Neither T_{50} nor T_{90} affected NO_x emissions. There was a small statistically significant interaction between ethanol and T_{50}. NO_x emissions tended to decrease as T_{50} increased when the fuel contained 10% ethanol, but not at 5.7% or in the absence of ethanol.

Reducing T_{50} reduced formaldehyde, benzene and 1,3 butadiene emissions, but did not affect acetaldehyde emissions.

Durbin et al. also evaluated the possibility of using Drivability Index to predict NMHC emissions. Not surprisingly, the correlation using the DI equation was not as precise as the regression equations in predicting NMHC emissions for the fleet of vehicles tested in this program. In the DI equation, the coefficients were determined to predict drivability not emissions, while in the emissions regression, the coefficients are determined to predict emissions. While the effects may be related, it is simplistic to assume that they will be exactly equal.

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A number of programs have been carried out in Europe to measure the emissions impact of mid-fill and back-end volatility. Jeffrey and Elliott [46] tested three catalyst vehicles (model years 1990 - 1992) with a set of 19 fuels in a factorial design. T_{90} varied between 110°C and 160°C. Lowering T_{90} from 160°C to 110°C reduced HC emissions by 17%, very similar to the 22% found for the 1989 model year U.S. vehicles in AQIRP. NO_x emissions tended to increase (16%), while the CO response was mixed. As in other similar programs, the authors recognized that some of the T_{90} effect could be due to variations in T_{50}, since the two were correlated.

Wedekind et al. [47] tested one catalyst car (early 90s vintage) with 11 fuels in which three levels of T_{50} and T_{90} were tested (85°C, 100°C, 115°C for T_{50} and 122°C, 141°C and 162°C for T_{90}). The variables were controlled independently. Volatility was adjusted while maintaining aromatic content constant by using lighter and heavier aromatic compounds as needed. As such, the impact of volatility cannot be separated from the effects of changing the distribution of aromatic molecular weights. The vehicle was tested using the European ECE/EUDC cycle where sampling is started after 40 seconds of idling. Reducing T_{50} from 115°C to 85°C reduced HC emissions less than 20% and CO emissions between 20-40%. NO_x emissions increased 20-40%. Reducing T_{90} from 160°C to 120°C lowered HC emissions 20-40% and raised NO_x emissions by 20-40%. CO emissions were unaffected.

CONCAWE conducted a program to determine whether the results seen in AQIRP for U.S. vehicles would be similar for European LD vehicles [72, 73]. Seven fuels had T_{90} levels between 145°C and 176°C. RVP and T_{50} values were held constant. The chemical composition of the back-end was also varied in the test fuel design. Aromatics varied in the range 38-50%, olefins in the range 0-9% and paraffins in the range 43-54%. Ten European LD vehicles were tested, all having TWC and fuel injection. HC and CO emissions increased by 9% and 14%, respectively when T_{90} increased from 140°C to 160°C, but did not change between 160°C and 180°C. NO_x emissions behaved in an opposite manner and were 5% lower when T_{90} increased versus the base level of 140°C. This behavior is similar in direction to the AQIRP results, but smaller in magnitude for HC. Also, the non-linearity seen in AQIRP results is different. Here, the lowest level of T_{90} provides the biggest effect. In AQIRP, changing T_{90} from the highest level provided the biggest benefits. The report recognized that assigning a specific volatility cut-point to an emissions effect was not a possibility because the parameters were not independent of each other. Within the range of T_{50} to T_{90}, it was not possible to ascribe the fuel effects to any one distillation point.

The EPEFE program [48] tested sixteen prototype vehicles designed to meet 1996 European emission limits. Aromatics and E70 were each tested at three levels in a nine-fuel factorial design. E100 targets were 35%, 50% and 65% corresponding to T_{50} values of approximately 85°C, 100°C and 120°C. The response of HC was non-linear, as seen in other programs. Stated in terms of T_{50}, at high levels of T_{50}, reducing T_{50} caused a large reduction in HC emissions, and at low levels of T_{50}, the impact was very small. Mid-fill volatility had little, if any, impact on CO and NO_x emissions.

Bennett et al. [49] tested three vehicles meeting Euro 1 emission standards (1993), and three vehicles meeting Euro 2 standards (1996). E100 varied between 49% and 58%, and E150 varied between 80% and 90%. No fuel effects were statistically significant, although the statistical power of the test was not clear.

McDonald et al. [50] studied aromatics and mid-fill volatility in twelve 1990-93 European catalyst cars. Three levels of T_{50} were tested (75°C, 95°C, 115°C), along with two levels of aromatics. They used the European ECE/EUDC test cycle. The authors did not present quantitative results for the impact of T_{50}, but showed that the results were very similar to those found in AQIRP studies.

Stradling et al. [28] tested three GDI cars and one MPI car with twelve fuels of varying volatility. The cars met Euro 3 or Euro 4 emission standards. Mid-fill and back-end were varied together. Reducing volatility had no consistent effect on NO_x or CO, and increased HC emissions for all the cars. When the final boiling point was reduced from 197°C to 176°C, HC emissions were reduced by 9% and CO emissions increased 20%. NO_x emissions increased in one car and did not change in the others.

Akimoto et al. [29] tested one 1993 Japanese vehicle with fuels having three levels of T_{50} (87°C to 104°C) and four levels of T_{90} (130°C to 163°C) that varied independently. They used the Japanese 10.15

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mode emissions test. T_{50} had no significant effect on any exhaust emission component. Reducing T_{90} lowered emissions of HC and CO, but did not affect NO_x emissions. No quantitative results were provided.

Saitoh and Hamasaki reported on the JCAP Program [32] in which three levels of T_{50} (72°C-124°C) and three levels of T_{90} (119°C – 183°C) were independently varied and tested in one stoichiometric MPI and two lean-burn GDI prototype vehicles. One of the GDI vehicles had a NO_x Storage Reduction catalyst. Two test cycles were used – the 10.15 mode (hot) and the 11 mode (cold). The results were inconsistent across the vehicles and the test modes; with the small number of vehicles tested, it was not possible to draw any general conclusions.

Koseki et al. [74] tested one 2004 model year MPI vehicle and one 2005 model year GDI vehicle – both stoichiometric - with fuels having two levels of T_{50} (92°C, 102°C) and T_{90} (145°C, 168°C). No impact of either variable was seen in the vehicles, although the statistical power of the test was not discussed.

Hirose et al. [56] measured particulate emissions in a 2005 model year lean-burn GDI Japanese car with nine fuels. T_{90} varied between 140°C and 166°C, and T_{50} varied between 89°C and 100°C in an independent manner. There was a statistically significant correlation between T_{90} and particle numbers in both the 10.15 and the 11 mode emission tests, with the coefficients being larger in the case of the 10.15 mode test.

Thummadetsak et al. [33] tested six cars representative of the Thai market (model years 1993-96) with two fuels having T_{50} levels of 95°C and 105°C. Four cars had TWC, one had an oxidation catalyst and one had no catalyst. The effects of reducing T_{50} were relatively small, and the only statistically significant change was a reduction in benzene exhaust emissions of 8.4%. It is possible that the relatively small change in T_{50} prevented identification of other effects.

In 1995 CONCAWE [75] published a thorough literature review and analysis of studies that measured the influence of mid-fill and back-end volatility on emissions. They compared studies to date from AQIRP, EPEFE, CONCAWE and others, and concluded that the preponderance of evidence suggested that mid-fill volatility was more important than back-end volatility. They found differences between U.S.-based AQUIRP and European-based CONCAWE programs on the influence of back-end composition on emissions (as opposed to back-end volatility). AQIRP [76] found no major impact while CONCAWE found some effects. The report was not able to account for these differences, except to point out that there were vehicle technology differences between the test fleets.

SUMMARY OF VOLATILITY EFFECTS

Most research has shown that reducing T_{50} and reducing T_{90} have similar effects – lower emissions of HC and CO and higher emissions of NO_x. Emissions of toxics and specific reactivity of emissions generally follow the HC emissions. The relative size of the effects of T_{50} and T_{90} has been somewhat variable, possibly reflecting details of the composition of the blendstocks used in the various programs. In the most recent CRC program [71], the fuels were blended with great care and the variables were almost perfectly orthogonal. While the T_{50} effect on HC was larger than the T_{90} effect, the results were difficult to interpret and included a number of interactions that were difficult to explain technically.

F. OXYGENATES (ETHERS AND ALCOHOLS)

Oxygenates are added to gasoline for a number of reasons, including enhancing octane, increasing volume and reducing petroleum use, limiting greenhouse gases, and reducing emissions. Oxygenates generally fall into two categories – alcohols and ethers. The lightest alcohol, methanol, once seriously considered, is rarely used today. Ethanol, the most common alcohol in use, can be made from biomass such as corn or sugar cane, and can reduce the emissions of greenhouse gases, depending on

the manufacturing process. This has been the subject of much scientific debate and will not be discussed here. Higher alcohols such as butanol (both normal and iso) have been considered, but are expensive and not available in as large quantities as ethanol. Ethanol can be used in all LD vehicles in the U.S. at concentrations up to 10%. In some Flexible Fuel Vehicles, it can be used at all concentrations between 0% and 85%. Ethanol has high octane and affects the volatility of the gasoline when it is splash blended - it increases the RVP of the gasoline base blend by up to 1 psi, and also lowers the T_{50} of the blend by up to 20°F (11°C).

The most common ether used in gasoline is MTBE (methyl *tertiary*-butyl ether), usually made by reacting methanol and isobutylene. Other ethers commonly considered for use are ETBE (ethyl *tertiary*-butyl ether) and TAME (*tetiary*-amyl methyl ether). ETBE is the analog of MTBE made with ethanol, and TAME is a reaction product of methanol and iso-pentene. Recently, ethers have been banned from use in gasoline in the U.S. because of concerns over groundwater contamination. MTBE is more soluble in water than gasoline and less biodegradable than ethanol. Leaks from underground tanks can result in MTBE penetrating into groundwater or drinking water supplies. While the health effects of MTBE are not fully defined, precaution dictates that ethers no longer be used in gasoline in the U.S.

Many of the studies cited below have concluded that the impact of oxygenates on exhaust emissions is a function of the oxygen content and the impact of the particular oxygenate on volatility, such as RVP or T_{50}. Therefore, in this section, all oxygenates will be considered together. Earlier studies tended to focus on ethers, while more recent studies have concentrated on the effects of ethanol, but a number of large studies have evaluated both. Hood and Farina [77] published a useful review in 1995 of oxygenate impacts, focusing on low ambient temperatures. This report incorporates many of the more recent (post-1990) references they cited.

AQIRP carried out a number of studies to evaluate oxygenates [41-43]. In the first study, MTBE was evaluated along with other variables in 20 1989 model year vehicles. Results comparing non-oxygenated gasoline and gasoline with 15% MTBE are shown below:

	Percent Change in Emissions MTBE 0% → 15%
NMHC	- 6.4
CO	- 11.1
NO$_x$	+ 1.4 (NS)
Specific Reactivity	+ 7.3
Benzene	- 5.5 (NS)
1,3 butadiene	- 8.8
Formaldehyde	+ 26.8
Acetaldehyde	- 1.9 (NS)

The addition of MTBE was accomplished while keeping all other variables constant. It was somewhat surprising that vehicles with good control of A/F ratio would still respond to the presence of oxygen. The effects were found to be the result of improvements in catalyst efficiency, not engine-out emissions, suggesting that stoichiometry over the catalyst was still somewhat variable. There were a number of interactions among the fuel variables, most notable between MTBE and aromatics with respect to NO$_x$ emissions. At low levels of aromatics (20%), addition of MTBE increased NO$_x$ emissions by 5%, while there was no effect at the higher level of aromatics (45%). This result is relevant because current aromatic levels are much closer to the lower end of the range studied than to the higher end, and the impact of oxygenates on NO$_x$ emissions has been somewhat inconsistent in other studies.

Addition of MTBE lowered exhaust emissions of 1,3 butadiene, probably because there were lower levels of paraffins, one of the main precursors to olefins in the exhaust. Formaldehyde emissions

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increased by 27%. Formaldehyde is a known partial combustion product of MTBE so this effect is not surprising. Analysis of the speciated exhaust also showed increased levels of isobutylene, another partial combustion product of MTBE. The increase of a highly reactive light olefin and formaldehyde probably accounted for the increased ozone reactivity seen with MTBE.

In a follow-up AQIRP study [62], ethanol (0%, 10%), MTBE (0%, 15%) and ETBE (0%, 17%) were tested in ten 1989 vehicles.

	Percent Change in Emissions from Adding Oxygenate			
	Ethanol 0% → 10%	MTBE 0% → 15%	ETBE 0% → 17%	Average Effect
NMHC	- 5.9	- 7.0	- 6.3	- 6.3
CO	- 13.4	- 9.3	- 14.6	- 12.5
NO_x	+ 5.1	+ 3.6 (NS)	+ 5.5 (NS)	+ 4.8
Reactivity	- 1.4 (NS)	+ 4.4	+ 11.4	*
Benzene	- 11.5	- 11.1	- 8.1 (NS)	- 10.5
1,3 Butadiene	- 5.8	- 1.7 (NS)	- 3.8 (NS)	- 4.2
Formaldehyde	+ 19.3 (NS)	+ 15.8 (NS)	- 15.7 (NS)	+ 11.8 (NS)
Acetaldehyde	+ 159	- 0.9 (NS)	+ 254	*
* Results are statistically different from each other and cannot be averaged.				

The results above are very similar to those measured in the previous AQIRP study and show that, with a few exceptions, the effects of the three oxygenates are statistically indistinguishable. The formaldehyde results had high variability and no conclusions could be drawn, even though the changes were relatively large. Acetaldehyde emissions increased dramatically for ethanol and ETBE because acetaldehyde is a known partial combustion product of both compounds. In this experiment, adding oxygenates increased NO_x emissions by about 5%, while reducing NMHC by 6% and CO by 12%.

When AQIRP studied high emitters [10], the benefits of ethanol and MTBE in reducing HC and CO emissions were found to be a little larger than in normal emitters, and the increase in NO_x was found to be about double. These results are consistent with vehicles that are running somewhat rich.

AQIRP carried out a direct comparison of MTBE and TAME blended at the same oxygen level of 2 weight%, in ten 1989 model year vehicles [78]. Reinforcing the conclusion that all oxygenates behave in a similar fashion, exhaust emissions for the two fuels were the same, with one exception. The TAME fuel had 28% higher emissions of formaldehyde, which the authors attributed to its slightly higher boiling point compared to MTBE.

Kanehara et al. [70] tested three levels of MTBE (0, 7%, 15%) in three 1990 model year vehicles. Interestingly, they reported that HC increased with MTBE, while CO and NO_x effects were mixed for the three cars.

Jessup et al. [59] tested 0% and 15% MTBE in ten LD vehicles ranging from 1984-1990 model years, and reported that MTBE did not affect any of the emissions. They did not report the details of the statistical analysis so it is not possible to evaluate their findings.

Farina [79] carried out a carefully designed experiment comparing a base fuel with two other fuels containing either 15% splash blended MTBE or 15% of a splash blended paraffinic HC stream. The HC stream was a mixture of hexane isomers with a vapor pressure and boiling range almost equal to MTBE. Ten 1989-93 model year LD vehicles were tested and the results are shown below for the fleet averages:

	Percent Change in Emissions Compared to Base Fuel	
	Isomerate Blend	MTBE Blend
NMOG	- 10.5	- 11.8
CO	- 5.0 (NS)	- 13.0
NO$_x$	- 4.8 (NS)	- 4.1 (NS)
Reactivity	- 4.3	- 1.1 (NS)
Benzene	- 24.9	- 22.1
1,3 Butadiene	- 15.2	- 11.6
Formaldehyde	- 1.0 (NS)	+ 7.1 (NS)
Acetaldehyde	- 4.9 (NS)	- 8.2 (NS)

Both streams caused similar changes in emissions, except for the possible exception of CO emissions, which were lower for MTBE, and specific reactivity, which was lower for the isomerate. Since, a number of properties – aromatics and T$_{50}$ for example – change when the streams were splashed blended, it is not possible to say with certainty what caused the emissions effects. However, Farina concluded that the only effect that could be caused by oxygen was the reduction in CO, and that some of the other effects that have been credited to oxygenates, such as lower HC and higher NO$_x$ emissions, are probably due to these other changes.

As part of the development of the ARB Predictive Model in 2006, ExxonMobil presented data from on a study in 1999 with five LEV and ULEV cars [80]. Four fuels were tested, having different levels of MTBE (10%) and ethanol (7%, 10%), along with a base fuel. The only statistically significant effect was an increase in NO$_x$ emissions of up to 30% with the addition of oxygenates. Toyota also presented data on nine California vehicles (TLEV, LEV and ULEV) with four fuels containing 10% MTBE or 10% ethanol [81]. Compared to the fuel with MTBE, the ethanol containing fuel had 6% lower NMHC and 5.5% higher NO$_x$ emissions. In both programs, presented to ARB, details of the statistics were not presented and the main use of the data was to add to the existing database that ARB was using to develop their Predictive Model.

CRC's recent Project E-67 measured the effects of volatility and ethanol in twelve 2001-03 model year LD vehicles [71]. Three levels of ethanol were tested – 0%, 5.7% and 10% - in a fractional factorial statistical design. Emissions with a subset of fuels were speciated. In general ethanol did not affect NMHC emissions, the exception being at high levels of T$_{90}$ (355°F, 179°C). Ethanol had a non-linear effect on CO emissions. Adding 5.7% ethanol reduced CO emissions by about 20%, but further increase in ethanol concentration up to 10% did not reduce CO emissions any further. The addition of ethanol tended to increase NOx emissions, but the effect depended on the T$_{50}$ value of the fuel. At low levels of T$_{50}$ (195°F, 91°C), the increase was about 10%, while at high levels of T$_{50}$ (235°F, 113°C), the response was flat. With respect to toxics, increasing ethanol concentration from 0 to 10% increased emissions of acetaldehyde by 73%. Surprisingly, addition of ethanol also increased emissions of benzene by 18% and 1,3 Butadiene by 22%. There was a significant ethanol x T$_{50}$ interaction for NOx emissions. For low levels of T$_{50}$, adding 10% ethanol increased NO$_x$ emissions by 12%. For medium levels of T$_{50}$, they were about 5% higher, and for high levels of T$_{50}$, NO$_x$ emissions were unchanged when ethanol was added.

A number of studies have also been carried out in European and Japanese vehicles. Jeffrey and Elliott [46] tested the impact of MTBE using a number of AQIRP and European fuels with three TWC cars (1990-92 model year). Adding 15% MTBE reduced CO in all three cars by 9, 13 and 16%. HC was reduced in two cars by 13% and 11%, and NO$_x$ was not affected. These results were consistent with those from the AQIRP study.

Morgan et al. [25] tested 27 cars from Japan, Europe and Canada from model years 1989-91. MTBE was varied in a designed matrix of eight fuels. They concluded that 15% MTBE reduces emissions

of CO, to a lesser extent HC, and did not affect NO_x emissions. No statistical analysis or quantitative measures were provided.

Bennett et al. [66] tested five European cars (1992-94 model years) with two levels of MTBE (0%, 10%) at low and high RVP levels, and found that adding 10% MTBE when RVP was high reduced CO and NO_x emissions by 15% and 7%, respectively. At low RVP levels, adding MTBE did not affect emissions at all. In a later program, Bennett et al. [49] tested three Euro 1 cars and three Euro 2 cars with fuels having the same two levels of MTBE. They reported that the Euro 2 cars had higher benzene emissions when 10% MTBE was present. The benzene effect was unexplained.

Graupner et al. [82] carried out a series of tests on European vehicles and fuels with different oxygenates – MTBE, ETBE, TAME, TBA (*tertiary*-butyl alcohol) and ethanol. Fuels were carefully blended by replacing isoparaffins with oxygenates, so as to minimize other changes. They concluded that for European catalyst vehicles, adding oxygenates reduced CO by a substantial amount (13%), reduced HC emissions by a smaller amount (5%), and had little or no effect on NO_x emissions. As in the AQIRP study, the response of individual vehicles was variable and there were no differences among the various oxygenates tested. They were also able to conclude, based on the way in which the fuels were blended, that the effects were most likely caused by the presence of oxygen in the molecules, and not by other physical or chemical properties.

Kwon et al. [27] tested a GDI car meeting the Euro 2 emission standards with two levels of MTBE, 0% and 10%, and found no statistically significant fuel effect.

Pentikainen et al. [60] compared fuels containing mixed ethers (MTBE, TAME) at 2% oxygen with ethanol at 3.5% oxygen. Twelve cars (1999-2002 model years) representative of the Finnish market were tested. No differences were measured in THC, CO and NO_x emissions. The ethanol fuel had higher emissions of 1,3 butadiene, benzene, and acetaldehyde, and lower emissions of formaldehyde.

In Japan, Saitoh and Hamasaki [32] tested three fuels with 0%, 6% and 13% MTBE; all other properties were held constant. Four cars were tested – three lean-burn GDI and one stoichiometric MPI. The only statistically significant effect was a reduction in CO in one of the cars when MTBE was used.

As part of the JCAP program, the impact of ETBE on emissions was tested and reported by Koseki et al. [83]. Three fuels were tested – 0%, 8% and 17% splash blended ETBE – in six cars and six motorcycles. The cars had emission levels at or below the 2005 standards. Five were standard MPI and one was GDI. Four motorcycles had 2-stroke engines and two had 4-stroke engines. Emission levels ranged from pre-1998 to post-1999, and one had an oxidation catalyst. Two Japanese test cycles were used for the cars – the 10.15 mode (hot test) and the 11 mode (cold test). The motorcycles used the Japanese motorcycle emission test. For the cars, there was no impact of ETBE at either level on emissions of HC, CO or NO_x. Acetaldehyde emissions tended to increase with the addition of ETBE but the effect was not statistically significant. For the motorcycles, adding 17% ETBE caused a statistically significant reduction in CO emissions in four of the six motorcycles. Acetaldehyde emissions increase significantly at both levels of ETBE in all six motorcycles. The authors did not present details of the analysis or tabulate the quantitative results.

In a follow-up study, JCAP studied 8% and 16% ETBE along with 3% ethanol in two low emission Japanese cars [74]. One had standard stoichiometric MPI and the other was a stoichiometric GDI engine. Both had emission levels that were 50% of the 2005 Japanese standard. All fuels were blended to have controlled properties. Almost all comparisons showed that there was not a significant difference in emissions when ETBE or ethanol was used in either car. The authors concluded that ETBE or ethanol could be used without adverse effects.

JCAP [55, 84] also reported on unregulated emissions in one model year 2003 lean-burn GDI car, containing a NSR catalyst for NO_x reduction. Three gasolines were tested - non-oxygenated, 8% ETBE and 3% ethanol. All other properties were the same for the three fuels. Speciated gaseous emissions and PM (mass, numbers and particle size distribution) were measured. The only statistically significant differences measured was that the ETBE fuel had higher acetaldehyde emissions in the 11 mode cold start test, and the ethanol fuel had higher acetaldehyde emissions in the cold start JC08 test.

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Thummadetsak [33] compared MTBE (0%, 7.5%, 15%) and ethanol (0%, 7.5%, 15%) blended gasolines in six 1993-96 model year cars representing large market share in Thailand, using the European driving cycle. Results are shown below for the five catalyst equipped vehicles. These are consistent with other published work except for the impact of ethanol on formaldehyde emissions.

	Percent Change in Emissions			
	MTBE		Ethanol	
	0% → 7.5%	0% → 15%	0% → 7.5%	0% → 15%
THC	- 4.6 (NS)	- 7.1	- 8.5	- 6.2
CO	- 6.6 (NS)	- 16.8	- 23.2	- 31.9
NO_x	+ 7.0	+ 7.2	+ 10.7	+ 15.2
Benzene	- 4.0 (NS)	- 1.6 (NS)	- 5.1 (NS)	- 1.7
1,3 Butadiene	+ 26.7 (NS)	+ 55.1 (NS)	+ 4.2 (NS)	+ 3.4 (NS)
Formaldehyde	+ 36.3 (NS)	+ 20.1 (NS)	+ 28.9	+ 37.2
Acetaldehyde	- 16.4 (NS)	+ 18.3 (NS)	+ 90.7	+ 231.1

A number of studies have been carried out on two wheel vehicles. Subramanian et al. [85] tested four 2-stroke motor scooters and a 4-stroke motorcycle commonly sold in India. All met the Euro 2 emission standards. Non-oxygenated, 5% ethanol and 10% ethanol gasolines were tested. Addition of ethanol lowered HC and CO emissions, especially at higher mileages. At low mileage, emissions of CO and HC were higher with the ethanol fuels. While the authors attributed this to the effects of aging and deposit build-up on the scavenging process in 2-stroke engines, no data was brought to support this argument. The ethanol fuels had higher emissions of acetaldehyde on both types of engines. NO_x emissions were not reported because they are generally low with 2-stroke engines.

Jaroonjitsathian [86] tested two samples each of three 4-stroke motorcycle models meeting the Euro 2 emission standard and common in the Thai market. A non-oxygenated gasoline was compared to a splash blended 10% ethanol blend. THC emissions were lower with ethanol on five of the six vehicles. For all the vehicles, CO emissions were lower and NO_x emissions were higher.

SUMMARY OF OXYGENATE EFFECTS

In studies where composition and volatility were controlled, adding oxygenates to gasoline resulted in lower HC and CO emissions, even in cars with sophisticated engine control systems. Emissions of NO_x tended to increase, although this effect was not measured in all programs. There was generally no difference between different kinds of oxygenates – alcohols or ethers. The most recent data suggest that the CO effect is still relevant, but the HC effect might be smaller or even non-existent in the newest technology.

While overall toxic emissions may be lower when oxygenates are added to gasoline, oxygenates usually increase emissions of aldehydes, the specific aldehyde depends on the chemical structure of the oxygenate. MTBE increases formaldehyde emissions and ethanol increase emissions of acetaldehyde.

G. GASOLINE SUMMARY AND RESEARCH NEEDS

A great deal of high quality data exists to define the impact of gasoline composition on exhaust emissions from gasoline LD vehicles. Directional changes are summarized in the table below. Many of the compositional and volatility changes – except for sulfur and RVP – have both positive and negative impacts. Deciding which changes to implement for regulatory purposes requires knowledge of the

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environmental needs, a detailed description of the vehicle fleet and a modeling tool that will provide a quantitative estimate. The most up-to-date model is the Predictive Model developed by ARB. [1]

	To Reduce Emissions, Make the Directional Changes Shown Below							
	Aromatics	Benzene	Olefins	Sulfur	Oxygenates	RVP	T_{50}	T_{90}
HC	↓	*	↑	↓	↑	↓	↓	↓
CO	↓	*	↑	↓	↑	↓	↓	↓
NO$_x$	↑	*	↓	↓	↓	0	↑	↑
Toxics	↓	↓	↓	↓	#	*	↓	↓
PM	*	*	*	*	*	*	*	*
0 No effect								
* Data are lacking to estimate an effect								
# Data exist, but effect is variable								

Knowledge gaps which may be closed by additional research are defined below. To a great extent, decisions about future research depend on a number of factors, including:

- Environmental and regulatory requirements
- Development and implementation of new vehicle technology
- Advent of new fuels technology and blendstocks

Shown below are areas where existing data are sparse or non-existent and where additional data would help understand fuel effects. If new vehicle technology such as GDI is developed and implemented, then it is important to understand all fuel effects.

- Effects of fuel parameters on PM emissions. Currently, this is not a particularly important area because gasoline vehicle PM emissions are still a small portion of the total inventory, but could become more important as diesel PM emissions drop.
- Effects of RVP on emissions at all temperature levels.
- Better understanding of the relative impacts of mid-fill volatility, back-end volatility and composition on exhaust emissions.
- Long term effects of sulfur on aftertreatment components and exhaust emissions. This is probably not relevant for U.S., Europe and Japan, where sulfur levels are close to zero, but could be important for other regions as they consider future sulfur levels.

Appendix III contains a compilation of the number of vehicles and fuels tested in programs that evaluated various fuel properties. As shown in the table, very little recent data has been collected evaluating the effects of RVP and olefins on exhaust emissions. Furthermore, all the recent data on aromatics has been measured in GDI equipped vehicles. If these parameters are considered important, then additional data may be required before regulatory action is taken.

4. DIESEL FUEL

Emissions data on diesel vehicles is arranged chronologically by fuel property. LD and HD diesel engines are described separately for each fuel property. This allows a natural comparison between the two engine types. For LD vehicles, research carried out since 1980 is considered. For HD engines and vehicles, research since 1998 and not covered in the review article by Lee et al. [4] is considered.

When blending diesel fuel for emissions studies, it is especially hard to blend fuel sets in which all properties are varied independently. Properties such as aromatics, density and cetane are correlated in

the refinery streams typically used to make fully formulated diesel. A few studies have succeeded in separating these variables, but in many studies, the variables are not independent and the conclusions are therefore somewhat ambiguous. These three variables are considered together in this report.

Fluid physical properties such as density and viscosity play a role in diesel emissions, because they affect the way that fuel droplets form as they exit the injector nozzle. While density has been studied extensively – mostly in conjunction with aromatics and cetane – the effect of viscosity has not received much attention. This is likely because it is hard to control viscosity independently of other variables. Effects attributed to some of the more common variables, may, in fact, be caused by viscosity changes.

In the diesel cycle, combustion is initiated by compressing and heating the gas/liquid mixture in the combustion chamber where it ignites spontaneously in the absence of a spark. There are generally two combustion regimes. Homogeneous combustion is the burning of that portion of the fuel that has evaporated after exiting the fuel injector. Heterogeneous combustion involves burning at the fuel-vapor interface of the fuel droplets in the combustion chamber. The relative size of these two regimes is a function of engine operation and fuel properties, and can affect combustion chamber temperatures and emissions profiles. Some researchers have used this factor to help understand the impact of fuel properties on emissions.

The operation of diesel engines can be affected by fuel properties to a greater extent than in gasoline engines. For example, when fuel density changes, the volume of fuel injected to maintain the same power output also changes. Fuel density affects the timing and duration of injection, the onset and duration of combustion, and potentially the fraction of exhaust sent back to the combustion chamber through the EGR system. This complex relationship has been studied in a few research programs but is not fully understood. As diesel engines have become more sophisticated, with more electronic controls and feedback mechanisms, the relationships may change and should be studied more extensively.

Many studies have been carried out to evaluate specific fuels or fuel blendstocks – biodiesel, other oxygenates and Fischer Tropsch (FT) products. In most cases, these materials were splash blended into the diesel and no attempt was made to control fuel properties. While this approach may provide useful comparison information, it does not provide any understanding of how these materials affect emissions, and does not necessarily represent methods of future use.

Some papers and reports provided very limited information about the engines or vehicles that were tested. Minimum information should include make and model, along with year of production. Additional information about design features and emission standards would be helpful as well.

From a regulatory and environmental perspective, the important emissions from diesel engines are PM and NO_x. HC and CO emissions are low in diesel engines, and emission standards for HC and CO are rarely limiting on engine design. For this reason, some papers did not report HC and CO emissions. PM emissions have been measured in a number of different ways using different instruments and sampling conditions. As shown by Chang and Van Gerpen [87], sampling conditions such as dilution ratio and temperature profile of the exhaust affect the measured PM emissions. A number of different instruments exist to measure and speciate PM emissions, and recent effort has attempted to standardize measurement techniques. Some older publications contain data collected with sampling and measurement methodology that is different from today's common usage.

A number of excellent reviews have been published in recent years and are referenced in the appropriate sections. Among them are reviews by Rickeard et al. [88], Veinblatt et al. [89], Alleman and McCormick [90], and EPA [2, 91].

A common problem in evaluating effects and trends is the large amount of seemingly conflicting data. Some of the differences seen are real, some are due to poor experimental design involving non-orthogonal fuel sets and limited fleet size, and some are due to incomplete statistical analysis. The best way to solve some of these problems is to conduct a meta-analysis and develop a unified statistical model. This is a difficult analysis, considering the wide variety of technologies, test cycles and fuel parameters found in the literature. In 2001, EPA published such an analysis for HD diesels [2].

A. DENSITY, CETANE AND AROMATICS

Density, cetane and aromatics are discussed together because they are very closely associated with each other and because many research programs varied them together. In many programs, these variables are correlated and it is not possible to distinguish the effects of one over another. As discussed below, there is disagreement in the literature about which is the most important variable in terms affecting emissions.

Cetane is a measure of the combustion property of diesel fuel, somewhat analogous to octane in gasoline. Cetane measures the ability of the diesel fuel to auto-ignite under controlled temperature and pressure conditions. The major measure is the time delay from fuel injection to auto-ignition in a single cylinder engine, compared to a series of reference fuels. Cetane can also be raised by adding cetane improvers to diesel. The most common improvers are organic nitrates, such as ethyl hexyl nitrate. One important question has been whether cetane achieved though additization has the same emission properties as cetane achieved through HC blending.

From an emissions perspective, higher cetane numbers mean earlier onset of combustion; hence. more complete combustion, but potentially higher emissions of NO_x due to higher temperatures in the combustion chamber. Some research has questioned this line of reasoning, as discussed below.

Different measures of aromatics have been studied in the literature and the consensus is that the type of aromatics is at least as important as the amount of aromatics in total. A number of studies have examined the contribution of single ring aromatics (mono-aromatics) and multi-ring aromatics (di-, tri-aromatics, etc.) to emissions. Multi-ring aromatics are generically referred to as Polyaromatic Hydrocarbons (PAHs).

LIGHT DUTY DIESELS

Weidmann et al. [92] presented data on two Volkswagen Golfs tested with seven diesel fuels varying in volatility, density, aromatics and cetane number. Both vehicles were 1983 model year diesels with 1.6 liter indirect injection (IDI) engines – one was turbocharged and the other was naturally aspirated. The test cycle was the US FTP. The authors concluded that higher density fuels increased emissions of HC, CO, NO_x and PM. Unfortunately, there was a high degree of correlation between aromatics and density, and between cetane and density, so the exact cause of the effects could not be determined with any certainty.

Betts et al. [93] tested 37 fuels in three IDI cars. One was a production vehicle and the other two were prototypes. The production car had EGR but no aftertreatment, while the other two cars had oxidation catalysts. The production vehicle met 1993 European emission standards. Fuels were blended for three test phases. In the first, parameters varied were cetane, aromatics, back-end distillation (T_{95}), and density. In the second, sulfur was varied between 2 ppm and 2200 ppm. In the third, seven fuels were blended to reduce the correlation between density and aromatics that was present in the first phase. All fuels were tested in the production vehicle, and selected fuels were tested in the two prototypes to confirm earlier findings. The focus of the paper was particulates, and only some results were given for other emissions.

Based on the analysis of the data, fuel density was the most important fuel factor for PM emissions. and aromatics had no statistically significant impact. Two operating regions were described. In the first, density was within the vehicle's calibration value and the air-fuel ratio in the engine was high enough to assure essentially complete combustion. In this region, there was a linear relationship between density and PM emissions with a relatively small slope.

In the second operating region, high density caused overfueling and there was incomplete combustion because of localized regions of poor mixing in the combustion chamber. PM emissions increased rapidly, along with emissions of HC and CO. The response to density was 10 times higher in the overfueling region than in the normal operating region. The equations below show the relationships in both regions:

Normal operation: $PM = -0.464 + 0.558 \times Density + 0.00023 \times T_{95} + 0.022 \times Sulfur$

Overfueling: $PM = -4.11 + 6.18 \times Density + 0.00068 \times T_{95} - 0.0061 \times Cetane$

Ranges over which these equations were developed are shown below.

Property Range in Tested Fuels		
Property	Low	High
Density (g/ml)	0.81	0.87
Cetane	44	62
Aromatics (Vol. %)	10	35
Sulfur (ppm)	2	2200

In addition to impacting PM emissions in the overfueling region, increasing cetane also reduced HC emissions up to about 48 CN, above which the response was relatively flat.

The same authors [94] carried out further tests using fuels from the same set, on a catalyst equipped version of the vehicle described above, designed to meet the 1996 European standards, and came to the same conclusion – that the most important factor for PM emissions was fuel density. While there was no correlation between density and total aromatics, the authors reported a strong correlation between density and multi-ring aromatics, and suggested that more research should be done to determine the contributions of multi-ring aromatics to PM emissions.

Tritthart et al. [95] reported that emissions varied with fuel properties in two diesel prototype cars with oxidation catalysts, turbochargers, EGR and electronic controls. One was direct injection and one was indirect injection. Emissions were measured over the US FTP the European NEDC and the Japanese 10.15 mode cycles. Seven fuels were tested; density varied between 0.826 and 0.845 along with aromatics, cetane, sulfur and T_{90}. While there were differences among the fuels tested, density, aromatics and cetane were highly correlated and the authors could not ascribe the effects to any one property.

Lange et al. [96] tested one car, a 1991-1993 model year vehicle with indirect injection, EGR, and an oxidation catalyst, meeting Euro 1 emission standards. Although fuel properties were highly correlated in the overall fuel set, the authors used pairwise comparisons to conclude that PM emissions were affected by density and polyaromatics, but not mono-aromatics. There were no significant NO_x effects.

Den Ouden et al. [97] published a summary of results on 22 European cars with 40 fuels, although not all cars were tested on all fuels. Twenty of the cars were indirect injection, and there was a mix of turbocharged/naturally aspirated, EGR and catalyst systems. A number of cars were tested with and without oxidation catalysts. Both European and U.S. emission test cycles were used across the fleet. Some of the data in this paper were part of a CONCAWE industry program. Only PM effects are discussed by Den Ouden et al., but CONCAWE [98] has discussed some of the same data and included gaseous emission results as well.

For the cars tested without catalysts, the most important fuel variable affecting PM emissions was density, and Den Ouden et al. developed the following relationship:

$$PM = A + \frac{B}{(C - Density)}$$

Polyaromatics were the second influential parameter, although of lesser importance than density. Cetane also seemed to have a small impact, reducing PM as cetane increased. Total aromatics did not influence PM emissions at all.

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When the same analysis was carried out for the catalyst vehicles, the impact of fuel properties was much less and no one parameter could be distinguished as most important. This was attributed to the fact that the oxidation catalyst reduces PM by oxidizing the fuel-based organic particulates. Other components of the total PM such as sulfate, soot and ash become a higher fraction of the total and these are not as closely related to the non-sulfur portion of the fuel.

In CONCAWE's analysis of gaseous emissions from six of the vehicles, increasing cetane reduced emissions of HC and CO. The effect was larger without oxidation catalysts in place. NO_x was not affected at all by fuel properties.

CONCAWE [99] carried out a series of experiments to answer the question about the influence of density on emissions: whether density differences cause changes in engine controls which therefore affect emissions, or whether some other mechanism causes the impact on emissions. They tested a 1992 model year European DI, 2.5 liter engine, with electronic injection control, oxidation catalyst and closed loop EGR. Two fuels, differing only in density, were tested. It was determined that fuel density affected the fuel pump setting, injection timing and EGR operation. With the advanced technology controls not in place, when engine operation was adjusted to compensate for the different fuel densities, the effect of changing densities on PM was almost totally removed (93%). When advanced technologies were in operation, only partial compensation was achieved (48%). The authors felt that the inability to achieve full compensation for density differences stemmed from their inability to fully control EGR operation in the advanced engine control unit (ECU). For NO_x, they achieved 43% compensation of the density effect, but there was some uncertainty about the correction to be used for humidity variations, and they felt that the level of compensation might be higher with an accurate correction.

Mann et al. [100] carried out a similar program with a 1995 model year DI engine with electronically controlled fuel injection, turbocharging and closed loop EGR. The vehicle was mounted in a test bed and a sophisticated adjustable controller was used to set engine operating parameters, such as injection timing and duration, EGR rate, boost pressure and boost temperature. Fourteen steady state modes were chosen to approximate the operating conditions of the European test cycle. The engine was operated with four fuels having different densities and PAH levels. (Viscosity varied with density, and can be considered a surrogate variable.) The density change increased EGR rate and advanced injection timing. Emissions were measured with normal engine operations and when these operating changes were reversed. The impact of density on emissions is shown below. Except for CO, the impact of density on emissions is reduced by at least half, when operations are adjusted for the different fuel properties. The authors argued that some of the EPEFE results described below, where there was a large variation in individual vehicles' response to changes in fuel properties, could be explained by differences in calibration strategies for the engine control algorithms.

	Percent Change in Emissions Density: 0.86 g/ml → 0.83 g/ml	
	Normal Tune	Controlled Tune
HC	- 7%	+ 3%
CO	- 7%	- 8%
NO_x	+ 8%	- 4%
PM	- 12%	- 5%

This work was further extended by Kwon et al. [101] to other properties including cetane and aromatics. In order to collect more data, only four steady state modes were tested. Only results for the controlled tune case were presented in the paper, as shown below. In the fuel set, T_{95} and density were highly correlated, so that it is not possible to determine whether the effect shown below is caused by changes in density or T_{95}.

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Percent Change in Emissions			
Density Change (- 0.03 g/ml)	CN Change (+ 10 CN)	Mono Aromatics (- 7%)	Poly-aromatics (- 7%)
HC	- 7%	- 7%	0	+ 3%
CO	- 15%	- 17%	0	+ 2%
NO$_x$	- 2%	- 3%	- 1%	- 3%
PM	- 14%	+ 3%	- 4%	- 9%

Since the authors did not provide the impact of fuel properties in the vehicles in the absence of special adjustments, it is not possible to evaluate the importance of compensation in this program. It is also difficult to generalize from the results in one vehicle to project how important this effect is in the general population.

Tsurutani et al. [102] tested one Japanese car - a Toyota Corolla with a naturally aspirated 2 liter engine, with EGR but no catalyst – with 45 different fuels. These included fully blended fuels, narrow boiling fuels, cetane improved fuels and splash blended fuels. For the splash blended HC fuels, 5% of individual compounds were added. Paraffin compounds were n-octadecane ($C_{18}H_{38}$) and n-eicosane ($C_{20}H_{42}$). The mono-aromatic was dodecylbenzene ($C_{18}H_{30}$), the di-aromatic was naphthalene ($C_{10}H_8$) and the tri-aromatic was phenanthrene ($C_{14}H_{10}$). The volatility properties are similar and small amounts were used, so other fuel properties did not change and it was possible to determine the effects of heavy aromatics. European and Japanese test cycles were used.

NOx emissions were reduced when total aromatics were lowered. Neither cetane nor total aromatics had any effect on PM emissions. Cetane improver lowered PM emissions when starting from a relatively low value (46 CN). The fuels in which 5% of individual compounds were added showed that di- and tri-aromatics are important contributors to PM emissions, as shown below.

Added Compound (5% each)	Percent Change in PM Emissions
n-octadecane	- 1
n-eicosane	+ 2
dodecylbenzene	+ 3
naphthalene	+ 14
phenanthrene	+ 22

It is clear from these data that paraffins and total aromatics do not have a compositional effect on PM emissions, and that polyaromatic compounds increase PM emissions. Regression analysis showed that the relative contribution of mono-aromatics/di-aromatics/tri-aromatics was 1/4/5.

Although the results were not analyzed in terms of density, fuel density was correlated with aromatics, T$_{90}$ and to a lesser extent cetane, in the fuel set. Therefore, any conclusions about total aromatics and density may be somewhat ambiguous.

The EPEFE program was a large, well-designed program that tested 19 LD diesel vehicles with eleven fuels [103]. The vehicles consisted of 17 passenger cars and 2 LD trucks, and contained a mix of DI and IDI, naturally aspirated and turbocharged, electronic and mechanical injection systems. All the vehicles had oxidation catalysts, and met the relevant European 1996 emission standards. The fuels were blended from refinery streams and consisted of three sets designed to determine the first order

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(linear) impacts of density, polyaromatics, cetane, and back-end volatility measured as T_{95}. The European driving cycle was used. The impacts on fleet average emissions are shown below:

	Percent Change in Emissions		
	Density (g/ml) 0.855 → 0.820	PAH 8% → 1%	Cetane 51 → 58
HC	- 18	+ 5.5	- 25
CO	- 16	+ 4	- 26
NO$_x$	+ 2	- 3.3	0
PM	- 19	- 5	+ 5

As in other large fleet tests, there were differences, mostly in magnitude and not direction, among the vehicles in response to fuel properties. Vehicles with electronic injection systems (mostly DI) were generally more sensitive to fuel property changes than those with mechanically controlled injection systems (mostly IDI), except for NO$_x$ where the reverse was true. One difference was that increasing cetane reduced NOx in the DI vehicles and increased NO$_x$ in the IDI vehicles. Speciated emissions were measured but too few tests were carried out to allow a meaningful statistical analysis.

An additional experiment was carried out in which engine tuning was adjusted for different density fuels. The response of emissions to density was reduced, but not eliminated, when engine calibrations were changed to match densities on three of the more advanced vehicles. The authors were not certain whether there is some residual effect that did not respond to calibration adjustment or whether further refinement of the calibration would eliminate the density effect totally.

As a follow-up to the EPEFE program, CONCAWE [104] tested three diesel cars equipped with DI, turbocharged engines. Emissions were controlled with EGR and oxidation catalysts. One car had a rotary pump, the second had a common rail injection system, and the third had unit injectors. Although built to meet Euro 2 emission standards, the cars had emission levels at or near Euro 3 standards. Eleven fuels were carefully blended in two matrices to study cetane (natural and additized) and aromatics composition. Results are summarized below for the average responses. Increasing cetane number had no measurable effect on NO$_x$ and PM, and reduced THC and CO emissions. There was no difference between natural and additized cetane. Reducing aromatics only affected CO emissions. No difference was seen between the effect of mono-aromatics and poly-aromatics. The differences between these results and those obtained in EPEFE were noted, and might be due to the differences in technology or to the small number of vehicles tested in this study.

	Percent Change in Emissions	
	Cetane Number 49 → 58	Total Aromatics 30% → 12%
HC	- 15	NS
CO	- 50	- 10
NO$_x$	NS	NS
PM	NS	NS

Tamanouchi et al. [105] tested two 1992 model year cars made for sale in Europe on fuels with varying levels of di- and tri-aromatics. Both cars had IDI engines, with turbochargers and oxidation catalysts. PAH concentration varied between 0.7% and 12.4%. The authors concluded that reducing PAH lowers emissions of THC, CO and PM, and that the effect was smaller when oxidation catalysts were in place, although no quantitative results are discussed and no statistics are provided.

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Oyama and Kakegawa [106] reported the results of Phase 1 of JCAP in which 13 fuels were tested with 14 LD vehicles meeting either 1990-94 or 1997-99 emission regulations. Results were not presented in a quantitative fashion, but the study concluded that lower aromatics reduced PM, and NO_x was unchanged. Within the aromatics, tri-aromatics had a larger impact than di-aromatics, which had a larger impact than mono-aromatics.

In the second Phase of JCAP [107], three diesel cars with advanced aftertreatment were tested. One had a NO_x Storage Reduction (NSR) catalyst, one had a DPF and one had both. All three had electronic injection control and two of them had common rail fuel distribution. Emissions levels were half of the 2003 Japanese standards. Fuel effects were generally small. When cetane was increased from 47 to 54, PM emissions increased by 13% in one of the cars. Other effects were listed as less than 10% and not quantified in the paper.

JCAP [108, 109] also tested a LD DI diesel engine with common rail injection and equipped with a NSR catalyst, DPF and oxidation catalyst aftertreatment system. Reducing total aromatics from 19% to 5% reduced engine-out PM, THC, CO and NO_x emissions. Reducing aromatics reduced tailpipe NO_x emissions, but the effect on tailpipe PM, THC and CO could not be measured because of the extremely low levels of emissions. In a second series of tests, the effect of aromatics on NO_x did not show a clear trend.

Nakakita et al. [110] tested ten carefully blended fuels in three single cylinder diesel engines, one of which had an optical port to allow spectroscopic measurements. The molecular structure of the fuels was carefully controlled to evaluate chemical composition, including ring structure and paraffinic content. Emissions were measured at a number of steady state conditions. Nakakita et al. concluded that under low and medium load conditions, cycloparaffins (naphthenes) have a higher PM formation tendency than paraffins, and that all aromatics have a higher PM formation tendency than paraffins. Two-ring aromatics showed a higher PM forming tendencytendency than one-ring aromatics. When cetane values were very high, leading to short ignition delay, PM emissions tended to be higher.

Bielaczyc et al. [111] tested one LD diesel car meeting Euro 3 emission standards with fuels having cetane number between 45 and 63. The engine was 2.0 liter, DI, common rail injection, turbocharged, with closed loop EGR and an oxidation catalyst. The European NEDC test cycle was used. Increasing cetane number reduced emissions of HC, CO and NO_x. The effect seemed to be larger when the cetane number was above 50. On the other hand, PM increased up to 55 CN and stayed relatively constant above that level. No statistics were provided for this analysis, which is not fully consistent with other test results. However, even if the results are statistically significant, tests on a single vehicle cannot be used to generalize trends.

HEAVY DUTY DIESELS

In a review of work published prior to 1998, Lee et al. [4] summarized fuel impacts on HD diesel engines. The summary is shown below for what were described at the time as "low emission engines."

	Change in Emissions		
	Reduce Density	Reduce Aromatics/PAH	Increase Cetane
HC	↑	0/↓	0
CO	↑	0/0	0
NO_x	↓	↓/↓	↓
PM	0	0/0	0

Lee did not attempt to carry out a full analysis of all the previous work but attempted to identify common trends. One of the main research programs relied upon by Lee was the EPEFE program on HD diesels [112].

Ryan et al. [113] tested one HD engine with thirteen fuels varying in natural cetane, additized cetane, total aromatics, and aromatics type. The engine was a Caterpillar 3176B model, with electronic unit injectors. It was tested without EGR to simulate the 1994 emissions standards and with EGR to simulate an engine meeting 2004 emission standards. Seven steady state modes were averaged to approximate the FTP transient test. PM emissions were measured at only two of the modes.

The range of variables is shown below:

	Min.	Max.
Aromatics, vol. %	9.5	30.9
Di-aromatics, vol. %	0.5	7
Density, g/ml	0.8131	0.8636
Cetane	35.9	56.3

A graphical analysis did not show any relationship between fuel properties and emissions for either engine configuration. A regression analysis showed that there were some significant variables – NO_x was correlated with aromatic type, and HC were negatively correlated with cetane. The correlations were in general very weak and did not explain much of the variability. In addition, no data were provided on the amount of correlation between variables.

Tanaka et al. [114] tested one HD, large volume Japanese engine with 28 fuels. It was an 8 liter DI, turbocharged engine with no EGR or aftertreatment, meeting 1994 Japanese emission standards. The Japanese 13 mode cycle was used for testing emissions. Low sulfur blends and kerosene blends were tested, but properties did not vary in a way that would allow any conclusions about effects of individual properties. Sixteen fuels were blended to vary concentrations of mono-aromatics, di-aromatics, tri-aromatics, and naphthenes. In addition to changes in aromatic concentrations, there were also attendant changes in density. Although the conclusions are stated in terms of aromatics, it is possible that effects of density are confounding the results.

There was a strong correlation between emissions of individual PAH compounds and tri-aromatics in the fuel, and weaker correlations with other classes of aromatics. The authors suggested that the influence of tri-aromatics in the fuel on PAH emissions was promoted by the presence of di-aromatics, mono-aromatics and naphthenes. In the absence of tri-aromatics, these other classes would not impact PAH emissions.

The USEPA Heavy Duty Emissions Work Group [115, 116] (HDEWG) tested a HD engine that was representative of 1994-1997 technology and was designed to meet strict NO_x emission standards. It was a 10.3 liter, DI, turbocharged engine with central electronic injection control and EGR. Eight steady state test conditions were chosen to provide good correlation to the FTP. Eighteen fuels varying in cetane, density, mono-aromatic content and PAH content were blended in a fractional factorial design with excellent orthogonality in the design variables. PM emissions were not reported. Regression analysis showed the following significant effects:

Percent Change in Emissions			
Density (g/ml) (0.86 → 0.83)	Mono-Aromatics (25% → 10%)	Poly-aromatics (11% → 3%)	Cetane (45 → 52)

	Density (g/ml) (0.86 → 0.83)	Mono-Aromatics (25% → 10%)	Poly-aromatics (11% → 3%)	Cetane (45 → 52)
HC	NS	- 6.4%	- 7.4%	- 12.4%
CO	NS	NS	NS	- 13%
NO$_x$	- 4.7%	- 3.7%	- 2.2%	+ 1.3%

There were no significant differences between natural and additive-based cetane.

Mitchell [117] reported on a Canadian program that tested four HD engines with fifteen fuels. One engine was the same one as tested in the EPA HDWG program described above. The focus of the program was to compare fuels prepared from oil sands with those prepared from crude oil, but three levels of aromatics were also evaluated (10%, 20%, and 30%). The program concluded that NO$_x$ emissions were best predicted by aromatics. While cetane number affected NO$_x$ emissions in each of the engines, the effect was in opposite direction for the engines. Fuel density had an effect on PM in two engines, but did not in the others. A further complication in understanding the results was that there was a strong correlation between aromatics and density in the fuel set.

JCAP [106] tested eight truck engines with sizes ranging from 3.6 to 21 liters. Seven were DI, three were turbocharged, one had mechanical injection and three had EGR. They were chosen to represent the existing Japanese truck fleet meeting 1990-1994 or 1997-1999 emission standards. The Japanese 13 mode test was used. For these engines, five fuels varying in T$_{90}$ and aromatics were tested.

Regression analysis showed that reducing aromatics lowered NO$_x$ emissions (~0.5%NOx/%aromatics) and had a variable effect on PM emissions. In this fuel set, however, there was a strong correlation (0.9) between total aromatics and PAH, so it is not possible to ascribe the aromatics effects to total aromatics alone. There was also a correlation between aromatics and density (~0.6) and cetane number (- 0.7) that may confound the analysis.

In the second part of the program, called the Model Step, two engines representing 1997-1999 emissions regulations were tested with nine fuels varying in types of aromatics, T$_{90}$ and sulfur. Density and cetane were held within a narrow range and the design variables had low levels of correlation among them. Aromatic type had a very marked effect on PM, with tri-aromatics having a larger impact than di-aromatics and mono-aromatics (5/2/1). Effects on NO$_x$ were mixed, as in the previous experiment.

JCAP II evaluated advanced diesel technology [107]. Three truck engines varying in size from 3.8 liter to 15.7 liter were tested in 14 fuels using the 13 mode emissions test. Three aftertreatment systems were tested – DPF, DPF with Urea-SCR, and NSR. Emission levels were targeted to be ½ the 2003 Japanese standards. They reported that between values of 47 and 54, cetane number had no impact on NOx or PM emissions.

JCAP II evaluated NOx emissions with a Urea-SCR aftertreatment system in a 13 liter engine with unit injectors and no EGR [108]. Three aromatic levels (5%, 9%, and 19%) were tested using the D13 emissions cycle. Density was held constant, but cetane number varied between 57 and 63. No impact of aromatics was seen on NO$_x$ emissions with the Urea-SCR system in place.

Using the same fuel set, JCAP II tested a 9 liter DI turbocharged engine having a common rail injection, EGR and a Urea-SCR/DPF aftertreatment system. Two test cycles were used – steady state D13 and transient JC05. The only emissions component affected by aromatics content was PM. As aromatics were reduced, engine-out PM decreased. Tailpipe emissions were so low with the DPF that effects were hard to determine.

JCAP [55] measured PM numbers and size distribution in a 9 liter turbocharged engine with EGR and Urea-SCR aftertreatment. The engine met 2005 emission standards. No PM emission differences were seen between fuels having 10% and 18% aromatics.

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Khalek et al. [118] tested two 1997/98 model year HD engines with fourteen fuels. One engine was a 6 liter, turbocharged engine with a mechanical injection system. The other was a 12.7 liter, turbocharged engine with unit injectors. Neither engine had aftertreatment systems or EGR. The hot start EPA transient test was used. The fuels varied in cetane number, sulfur and aromatics (total and PAH). T_{90} also varied, but was not reported in the results. The objective of the program was to develop low emissions fuels, but some regression analyses were shown. The responses that were similar for both engines are shown below. Regression results were not reported for cells that are blank.

	Percent Change in Emissions (Average of 2 engines)		
	Total Aromatics (25% → 15%)	Poly-aromatics (11% → 3%)	Cetane (49 → 63)
HC			- 28%
CO			
NO$_x$	- 7%		- 6%
PM	NS	NS	NS

As a follow-up to the EPEFE program, CONCAWE [104] tested two HD European DI engines equipped with turbochargers. One engine had a high pressure inline pump with no EGR, and the other had unit injectors and a cooled EGR system. Neither engine had aftertreatment devices, and both were designed to meet the Euro 3 emission standards. Eleven fuels were carefully blended in two matrices to study cetane (natural and additized) and aromatics composition. The European Steady State Cycle (ESC) and European dynamic Load Response (ELR) test for smoke were used. Results are summarized below for the average responses. Increasing cetane number had no measurable effect on any of the emissions responses. There was no difference between natural and additized cetane. Reducing aromatics only affected HC emissions. No difference was seen between the effect of mono-aromatics and poly-aromatics. The differences between these results and those obtained in EPEFE were noted, and might be due to the differences in technology or to the small number of vehicles tested in this study.

	Percent Change in Emissions	
	Cetane Number 49 → 58	Total Aromatics 30% → 12%
HC	NS	- 20%
CO	NS	NS
NO$_x$	NS	NS
PM	NS	NS

Kono et al. [119] tested three Japanese DI engines with high pressure injection, two of which were turbocharged. All three had EGR, one had an oxidation catalyst, and one had a complex NSR/DPF aftertreatment system. The engines were designed for 2 ton cargo trucks; one met the 1998 Japanese standards, and the other two met the 2003 standards. All were tested using the JC08 emissions test, which involved both cold and hot start operation. Eight fuels were tested, three of which varied in aromatic levels (5%, 9%, 16%). Other properties such as density and cetane number varied as well in the fuel set, so it is not possible to unambiguously assign effects to individual properties. No detailed analysis is presented, but the authors reported that fuel effects on NO$_x$ and PM were small (less than 5%). With the DPF engine, the emissions were too low to be able to discern any fuel effect. They did not report any effects of aromatics on HC or CO.

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The engine with the oxidation catalyst was tested on the same set of fuels with a number of different driving cycles including the JC08, JE05 (HD cycle), USFTP, USHFET, TMG (Japanese city driving). Further statistical analysis was also carried out with respect to non-design variables. Kono et al. concluded that di-aromatics increased PM emissions and the soot component of these emissions. Higher levels of Cetane Index, but not cetane, was found to reduce emissions of NO_x and THC. It was not clear why cetane index correlates with NO_x, and not cetane. Also, the authors acknowledge that there are significant correlations among the expanded set of fuel variables.

Massa et al. [120] tested two engines commonly used in buses in Brazil. Both were naturally aspirated engines, about 4 liter displacement, with no EGR or aftertreatment and contain Euro 3 technology. One had a common rail injection system and the other had unit injectors. Six fuels were tested, varying in cetane between 42 and 48, achieved through blending and with additives. Other properties were held constant. Analysis of Variance showed that there were no significant effects of cetane on exhaust emissions of HC, CO, NO_x or PM.

SUMMARY OF EFFECTS OF AROMATICS, CETANE, DENSITY

Taken together, the fuel properties of density, aromatics, especially PAH, and cetane have been shown to affect diesel emissions, although contradictory results have been published, as described in some detail by Kono et al. [121]. A number of factors combine to make the literature difficult to summarize:

- Lack of orthogonality among variables in many studies.
- Small number of vehicles/engines tested in many programs combined with high variability in vehicle response makes comparisons difficult, because different results are to be expected.
- Different test cycles have been used, some of them representing steady state conditions and some representing transient, some containing cold start driving and some containing only hot start driving.

With these caveats in mind, the following tables are meant to provide a general consensus of research for LD and HD diesels.

	Change in Emissions – Light Duty Diesels		
	Reduce Density	Reduce PAH	Increase Cetane
HC	↓	↑	↓
CO	↓	↑	↓
NO_x	—	↓	
PM	↓	↓	↑

The table above shows only PAH, not total aromatics. It seems likely that the impact of aromatics is caused to a greater extent by the multi-ring aromatics than by the single ring aromatics.

The LD effects are for vehicles without aftertreatment. The effects seem to be smaller and more difficult to measure with aftertreatment systems in place. They can also be different. Oxidation catalysts oxidize the organic fraction of PM, so that PAH, which may contribute to this fraction, would have less of an impact with oxidation catalysts in place. All PM effects are small and difficult to measure with DPF in place. LD diesels have also been studied to understand the impact of fuel properties on engine operation. As technology develops, it is expected that engine operation will be increasingly controlled by feedback control mechanisms, and the impacts of fuel properties may change.

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Finally, development and deployment of new aftertreatment devices to meet strict emissions standards may also change the responses.

A summary table for HD diesels is shown below:

	Change in Emissions – Heavy Duty Diesels		
	Reduce Density	Reduce PAH	Increase Cetane
HC		↓	↓
CO			↓
NO$_x$	↓	↓	
PM		↓	

Reducing density lowers NO$_x$ emissions, and reducing PAH content lowers NO$_x$ and PM emissions, while increasing cetane lowers HC and CO emissions; but there is some evidence that in modern engines, PM emissions may increase, as seen more often in LD diesels. As engines become more sophisticated in terms of injection control, fuel effects on emissions seem to be lessened. This is especially true for DPF systems that have a very high efficiency for PM reduction and are probably not much affected by changes in PAH content.

More data should be obtained on a wide variety of diesels with aftertreatment systems such as Urea-SCR and/or NSR catalysts using the latest test cycles which employ transient and cold start driving patterns.

B. SULFUR

Under combustion conditions, sulfur compounds in diesel fuel burn mostly to form the gas sulfur dioxide. A relatively small fraction (1%-2%) is oxidized further to sulfur trioxide or sulfuric acid, which may associate with water molecules or dissolve in liquid water. The fraction of sulfur that is emitted as sulfate also depends on the temperature and oxygen content of the gas stream. Sulfur in diesel fuel can affect emissions in two ways. First, sulfates in the exhaust may react with other components in the exhaust to form solid sulfate particles. Sulfuric acid droplets may act as nucleation sites for particle formation and growth. Sulfur dioxide in the exhaust can be further oxidized over certain catalysts to form additional sulfate particles.

Diesel sulfur may also affect emissions by degrading the operation of various aftertreatment devices. NO$_x$ catalysts, especially storage devices are particularly sensitive to sulfur and lose efficiency as sulfur rises to 50 ppm and above. Diesel particulate filters are also somewhat sensitive to sulfur and in addition to reducing efficiency, high sulfur levels may also cause overall fuel economy to suffer when the filter needs to regenerate more often.

The effect of sulfur is relatively easy to study, since sulfur levels can be changed without impacting other properties. Earlier work focused on the impact of sulfur on particulate mass and composition, and more recent work has evaluated the impact of sulfur on aftertreatment devices. When typical diesel sulfur levels were 2000 ppm or more, reducing the sulfur content of diesel fuel could have a direct impact on PM emissions. However, at levels of 500 ppm and below, the impact of changes in sulfur concentration on PM emissions is fairly small.

LIGHT DUTY DIESELS

Betts et al. [93] and Fløysand et al. [94] tested a European car with and without an oxidation catalyst. The car had an IDI engine with EGR and met the European 1993 emission standards in the

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non-catalyst configuration. Sulfur had a weak but measurable effect on total PM emissions, and the effect was slightly larger with the oxidation catalyst.

Percent change in PM Emissions 2000 ppm S → 100 ppm S	
Without Catalyst	With Catalyst
- 4.0	- 12.1

The National Renewable Energy Laboratory of the Department of Energy (NREL/DOE) sponsored DECSE (Diesel Emissions Control – Sulfur Effects Project), which studied sulfur effects in LD and HD diesel engines with advanced prototype aftertreatment systems. Results have been published in a number of papers and reports [122-124]. One LD vehicle was tested with a 1.9 liter prototype DaimlerChrysler engine and a NO_x Adsorber Catalyst system. The program measured catalyst efficiency and desulfurization effectiveness after aging with sulfur levels of 3, 16, 30 and 78 ppm. In general, with higher sulfur levels, the catalyst had to be regenerated more often. Results showed that at 30 ppm and below, desulfurization could restore efficiency to acceptable levels. After aging on 78 ppm sulfur, exposing the catalyst to repeated desulfurization procedures caused a decline in performance. This behavior was not observed with the fuels at or below 30 ppm. It is not known whether this is a feature of the specific catalyst tested or whether the behavior is more general.

JCAP [106] studied one car with two levels of sulfur, 0 ppm and 400 ppm. The engine was naturally aspirated IDI, 2.0 liter with EGR, and was tested with an oxidation catalyst. Relative to the high sulfur fuel, the zero sulfur fuel did not affect HC, CO or NO_x emissions, but did lower PM emissions by 45%. With the zero sulfur fuel, sulfate particulate in the exhaust disappeared, the soluble organic fraction (SOF) dropped by about 50% and dry soot more than doubled. Reasons for the impacts on SOF and soot were not explored.

Sluder and West [125, 126] tested a 1999 model year European Mercedes A170 diesel with fuels having sulfur levels of 3, 30 and 150 ppm. The engine was a turbocharged, DI design with EGR and two oxidation catalysts. Although not certified in the U.S., emissions fell within U.S. Tier 1 standards. In addition to the standard configuration, the vehicle was also tested separately with a catalyzed DPF and with a NO_x adsorber catalyst. Three test cycles were used – FTP, US06 and SC03.

In the range of sulfur tested, there was a small (<10%) effect on PM emissions. With the DPF in place, there was no degradation in emissions even for the highest sulfur fuel. PM emissions were so low (<0.006 g/mi) that background levels were 30%-50% of the measured values.

With a NOx adsorber catalyst in place, emissions of NO_x were very sensitive to sulfur. After the equivalent of 3,000 miles on 30 ppm sulfur, NO_x reduction efficiency went from 92% to 80% on the FTP and from 89% to 66% on the US06 cycle. Desulfurization cycles were not investigated.

Kwon et al. [101] evaluated sulfur effects with a 1995 model year European DI engine with electronic controlled fuel injection, turbocharging and closed loop EGR. The vehicle was mounted in a test bed and a sophisticated adjustable controller was used to set engine operating parameters, such as injection timing and duration, EGR rate, boost pressure and boost temperature. Fourteen steady state modes were chosen to approximate the operating conditions of the European test cycle. Reducing sulfur levels from 1000 ppm to zero reduced PM emissions by 13%. The same sulfur reduction also increased emissions of CO by 6%, although the specific doping compound used – t-butyl disulfide – may have been a factor.

Bielaczyc et al. [111] tested one LD diesel car meeting Euro 3 emission standards with four fuels having sulfur levels of <5, 50, 350 and 2000 ppm. The engine was 2.0 liter, DI, common rail injection, turbocharged, with closed loop EGR and an oxidation catalyst. The European NEDC test cycle was used. The biggest impact of sulfur was on PM emissions. The 2000 ppm fuel had PM emissions that were about 25% higher than any of the other fuels. Sulfur levels did not affect HC or CO emissions for

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the entire NEDC driving cycle, but there was a small mass effect in the EUDC portion of the cycle where catalyst temperatures are higher. Lower sulfur was associated with lower NO_x emissions, although the effect was smaller for NO_x than PM.

In the second Phase of JCAP [107] three modern diesel cars with advanced aftertreatment were tested. One had a NSR catalyst, one had a Diesel Particulate Filter (DPF) and one had both. All three had electronic injection control and two of them had common rail fuel distribution. Emissions levels were half of the 2003 Japanese standards. Five fuels were tested having sulfur levels of 10, 46, 94, 298 and 443 ppm. Both instantaneous emissions and mileage accumulation tests were carried out with different sulfur levels. Between 445 ppm and 45 ppm, changes in all emission levels were less than 10%. Reducing sulfur also appeared to result in increased levels of the soot component of PM emissions. For the vehicle containing a NSR catalyst, catalyst efficiency was significantly higher when using 10 ppm sulfur than when using 100 ppm sulfur for 30,000 km.

Ntziachristos et al. [40] reported results of the European Particulates project. Fourteen LD diesels were tested with four fuels having sulfur levels between 3 ppm and 280 ppm. Three were in the same base fuel (8, 38 and 280 ppm) and a fourth was Swedish Class 1 diesel (3 ppm) for reference. Most of the cars met or exceeded Euro 3 emission standards, and five were equipped with DPF aftertreatment. Over the range of sulfur levels studied, there were no effects of sulfur on PM mass emissions for vehicles with or without DPF. When considering particle numbers, the 280 ppm sulfur fuel had higher emissions than the other fuels, even with DPF. The higher numbers were due to increases in nucleation size particles (< 50 nm diameter).

JCAP [108] studied the impact of sulfur on a NSR-DPF catalyst system in a 4 liter LD DI engine, with cooled EGR and a common rail injector system. Three sulfur levels were tested: <1, 7 and 46 ppm. Two cycles were used for emissions evaluation – the steady state D13 and the transient JE05. Mileage was accumulated up to 50,000 km on all three test fuels. Desulfation intervals were geared to each fuel's sulfur concentration. After 50,000 km, there was a significant difference in catalyst efficiency when tested on the higher temperature D13 test. NO_x conversion efficiency was 85%, 78% and 60% for 1, 7 and 46 ppm, respectively. There did not appear to be a difference when tested using the JE05 cycle, which had conversion efficiencies of about 40%. By varying the desulfation intervals in a second series of tests, the authors were able to conclude that the main reason for loss of conversion efficiency is the heat generated during desulfation. Since lower sulfur fuel requires less frequent desulfation, conversion efficiency is maintained at a higher level when sulfur is low.

A passenger car was also tested on the same three fuels over the new Japanese emissions test cycle CD34 (JC08) as well as the older 10/15 mode test [109]. After 30,000 km, NO_x conversion efficiencies were 40-55% for the 46 ppm fuel, and 82-99% for the 1 ppm fuel, depending on test cycle. Fuel economy was 5% worse with 46 ppm sulfur than with 7 ppm sulfur fuels.

HEAVY DUTY DIESELS

Lee et al. [4] concluded that in the absence of aftertreatment, fuel sulfur only affected the sulfate portion of PM emissions.

Liang et al. [122] reported the results of DECSE tests with two DPF systems. One was a catalyzed DPF system (CDPF) and the other was a continuously regenerating DPF system (CR-DPF). All tests were conducted in a Cat 3126 engine, which is usually used in applications that result in low exhaust temperatures. This was considered a severe test for the DPF systems. Five sulfur levels were tested in a common fuel over the OICA 13 mode test cycle. On an engine-out basis, raising sulfur from 3 ppm to 350 ppm increased PM emissions by 29%. No changes were observed in the other emissions. The impact of sulfur on DPF efficiency is shown below:

	PM Efficiency*	
Fuel Sulfur	C-DPF	CR-DPF
3 ppm	95%	95 %
30 ppm	74%	72 %
150 ppm	0	- 3%
300 ppm	- 122%	- 155%
* Relative to engine-out emissions with 3 ppm sulfur fuel		

Efficiencies in the table above can be less than zero because the reference point is the emissions with 3 ppm sulfur fuel. Approximately 40-60% of the fuel sulfur was converted to sulfate, thereby increasing emissions when sulfur levels are high.

The DECSE program also tested lean NO_x catalysts in two engines, a Cummins ISM370 and a Navistar T444E [123]. The NO_x conversion was not affected significantly by changing sulfur levels but PM emissions were significantly affected. With 150 ppm and 350 ppm sulfur fuels, engine-out emissions of sulfate increased by a factor of 2-5, and tailpipe emissions of sulfate increased by a factor of 10-20. These increases are the result of oxidation of SO_2 to sulfate over the catalyst system.

Khalek et al. [118] tested two 1997/98 model year HD engines with fourteen fuels. One engine was a 6 liter, turbocharged engine with a mechanical injection system. The other was a 12.7 liter, turbocharged engine with unit injectors. Neither engine had aftertreatment systems or EGR. The hot start EPA transient test was conducted. When sulfur was reduced from 500 ppm to 50 ppm, the smaller engine had no response to sulfur content, while in the larger engine, PM emissions decreased by 15%. Other emissions were not affected.

In JCAP II [107] two truck engines with advanced aftertreatment were tested for sulfur effects. One engine had electronic injection control with EGR and a DPF. The other had common rail fuel distribution with no EGR and DPF+Urea/SCR aftertreatment system. Emission levels were half of the 2003 Japanese standards. Four fuels were tested having sulfur levels of 46, 94, 298 and 443 ppm. For mileage accumulation, fuels having sulfur levels of 9, 44 and 95 ppm were tested. Lowering sulfur reduced PM emissions in both engines and did not affect NO_x emissions. Mileage accumulation results were different for the two engines. For the engine with the DPF aftertreatment, higher sulfur levels increased backpressure over the DPF catalyst. After 30,000 km with 100 ppm sulfur, backpressure was 60 kPa, versus 20 kPa with 10 ppm fuel. The increased backpressure tended to raise the exhaust temperature and lower the conversion of NO to NO_2. The net effect was that there was no deterioration in PM emissions with 100 ppm fuel; however, fuel economy was reduced by 7% because of the higher backpressure. The second engine did not show any differences between the fuels over 10,000 km of mileage accumulation.

Frank et al. [127] tested a Navistar 2001 model year DT466E engine commonly used in urban transit buses with a variety of fuels and with a number of different aftertreatment configurations. Engine displacement was 7.6 liters, and the engine was turbocharged with electronically controlled injection, and no EGR. Although the fuel properties were not well designed to determine effects of individual properties, three different sulfur levels were blended with other properties held relatively constant. With an oxidation catalyst installed, both engine-out and tailpipe emissions were reported for fuels with sulfur levels between 28 ppm and 410 ppm. Engine-out emissions were about 10% lower with 28 ppm sulfur than with 410 ppm sulfur. For the same fuels, tailpipe PM emissions were reduced about 50%. This reduction is probably a result of sulfate production over the oxidation catalyst, although no data were provided for PM components.

The cooperative European Particulates Project [128] tested ten HD European diesels, ranging from Euro 1 technology to prototype Euro 4 and Euro 5 emission levels. All engines were DI with high pressure injectors. Three engines had DPFs and two engines had Urea-SCR systems. Four levels of

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sulfur were tested in one base fuel (8, 38, 280 and 1550 ppm), although not all fuels were tested in all the engines. The European Steady State Cycle (ESC) and the European Transient Cycle (ETC) were used. Only particulates were measured.

Reducing sulfur generally reduced PM emissions. The Euro 4 engine with DPF and the Euro 5 engine with Urea-SCR gave similar PM mass emissions with 38 ppm and 8 ppm, suggesting that these devices might not be sensitive to sulfur over this range. There was also a significant difference between the test cycles. The ESC cycle generates much higher exhaust temperatures, and PM emissions were much more responsive to sulfur levels. Solid or carbonaceous particles were measured and were not sensitive to fuel sulfur levels. The impact of sulfur on particle number was large for the engines equipped with DPFs, where sulfur in the fuel contributes to nucleation mode particles in the exhaust downstream of the DPF. Evaluation of the particle size distribution confirmed that sulfur impacts particles below 30 nm much more than particles above 30 nm.

Kono et al. [129] tested a 4.8 liter naturally aspirated DI engine usually used in a 2 ton truck. It was equipped with common rail injection, EGR and an oxidation catalyst. Two of the fuels differed only in sulfur (7 ppm, 46 ppm). Eight different Japanese and U.S. driving cycles were used. Engine-out and tailpipe emissions were measured for all the driving cycles, and sulfur in the range studied had little or no impact on emissions.

SUMMARY OF SULFUR EFFECTS

The most direct effect of lowering sulfur is to reduce the sulfate portion of PM, without changing any of the other engine-out emission components. Lowering sulfur also reduces the number of particles, especially in the nanometer range (< 50 nm).

DPFs are not particularly sensitive to sulfur, but there is some evidence that higher sulfur levels can result in increased backpressure, which may affect fuel economy. PM levels are so low that effects are difficult to measure. However, there is some evidence that sulfur has a large measurable effect on PM numbers.

NSR catalysts have been shown to be sensitive to sulfur above 50 ppm, and possibly require sulfur levels much lower than that. Even when the operation of the NSR is not directly affected by sulfur, higher sulfur levels require more frequent regeneration and the high temperatures associated with regeneration may degrade long-term catalyst activity. Urea-SCR catalyst systems are less sensitive than NSR catalysts to sulfur levels.

C. BACK-END VOLATILITY

The amount of high boiling material is a key diesel property. Usually this is defined by T_{90} or T_{95} as measured in the ASTM D86 distillation test. Some researchers have used end-point to characterize back-end volatility.

LIGHT DUTY DIESELS

Betts et al. [93] and Fløysand et al. [94] tested a car with and without an oxidation catalyst. The car had a 2.1 liter IDI engine with EGR and met the European 1993 emission standards in the non-catalyst configuration. Sixteen fuels were tested in the non-catalyst configuration and nine with the catalyst in place. T_{95} was varied between 345°C and 370°C, along with aromatics, cetane and density. In either configuration, reducing T_{95} by 20°C reduced PM a statistically significant amount (6% - 7%). No results were shown for the influence on other exhaust components.

Tritthart et al. [95] tested two cars, one DI and one IDI, both with EGR, turbochargers and oxidation catalysts. Seven fuels were tested, with T_{90} varying between 307°C and 327°C, along with

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varying cetane, density, aromatics and sulfur. The authors concluded that they did not find a relationship between T_{90} and any of the emission components.

Lange et al. [96] tested one car, a 1991-1993 model year (Euro 1 emission standards), with indirect injection, EGR, and an oxidation catalyst. Twelve fuels were tested in total. Four of them differed in T_{90} (326°C to 350°C) and polyaromatics and could be used to estimate effects of those parameters. An analysis showed that T_{90} did not affect PM or NO_x. No results were shown for HC or CO.

Tsurutani et al. [102] tested one Japanese car - a Toyota Corolla with a naturally aspirated 2 liter engine, with EGR but no catalyst – with 45 different fuels. These included fully blended fuels, narrow boiling fuels, cetane improved fuels, and splash blended fuels. European and Japanese test cycles were used. Lowering T_{90} reduced PM emissions, although it was not possible to separate the physical effects (volatility) and chemical effects (polyaromatics). In addition, for some of the fuels, T_{90} and density were highly correlated.

The EPEFE program, described in more detail above, tested nineteen LD diesel vehicles with eleven fuels [103]. All vehicles had oxidation catalysts, and met the relevant European 1996 emission standards. The fuels were blended from refinery streams and consisted of three sets designed to determine the first order (linear) impacts of polyaromatics, density, cetane, and back-end volatility measured as T_{95}. The European driving cycle was used. The impact of T_{95} on fleet average emissions was calculated from 6 fuels that varied T_{95} independently of other parameters, and is shown below.

	Percent Change in Emissions T_{95}: 370°C → 325°C
HC	+ 3 (NS)
CO	- 2 (NS)
NO_x	+ 4.5
PM	- 6.7

Trends suggested that reducing T_{95} increased emissions of benzene and formaldehyde but too few tests were carried out to allow a meaningful statistical analysis.

Tamanouchi et al. [105] tested two 1992 model year cars made for sale in Europe on fuels with levels of T_{90} varying between 276°C and 336°C. Both cars had IDI engines, with turbochargers and oxidation catalysts. Lowering T_{90} reduced emissions of PM in both cars, reduced THC and CO in one of the cars and had no effect on NO_x. No quantitative results were discussed and no statistics were provided.

JCAP carried out a number of studies examining the effect of back-end volatility on emissions [106-109]. In the first phase, eight cars were tested on a variety of fuels, and it was determined that reducing T_{90} lowered PM emissions but did not have a consistent impact on HC, CO or NO_x. In the second phase of JCAP, more advanced vehicles were tested including those with aftertreatment: NO_x reduction catalysts (NSR and Urea-SCR) and PM filters. In most cases, reducing T_{90} lowered PM emissions. The situation with respect to HC, CO and NO_x is a bit more complex. In a number of vehicles, engine-out and/or tailpipe NO_x emissions increased. It was theorized that lower T_{90} prevented the fuel introduced into the combustion chamber during the pilot-injection from igniting. Another possibility is that subtle changes in fuels caused changes in the EGR rate, which affect NO_x.

Kwon et al. [101] adjusted engine operating parameters so that different fuels had the same injection and EGR behaviors. In the fuel set, T_{95} and density were correlated so it is not possible to ascribe effects to one property or the other. Results are shown below:

	Percent Change in Emissions Reduce T_{95} 40°C*
HC	- 7%
CO	- 15%
NO$_x$	- 2%
PM	- 14%
* Highly correlated with density.	

Nishiumi et al. [130] tested two levels of volatility and cetane in a passenger car and a small diesel engine. Both engines were about 2 liter displacement, turbocharged, with EGR and common rail injection systems. Four fuels were tested; two had a narrow boiling range and two had a wide boiling range. The narrow boiling range fuels had T_{90} values of 250°C along with T_{10} values of 220°C. The wide boiling range fuels had T_{90} of 325°C and T_{10} values of 235°C. Fuel properties were adjusted by distillation and changing the normal/iso-paraffin ratios. Results showed that reducing the boiling range lowered PM emissions by reducing the SOF portion of the particulates. From the analysis of the fuels and the SOF in the particulates, it was determined that the presence of HC heavier than C_{18} contribute to SOF in the particulates.

HEAVY DUTY DIESELS

Lee et al. [4] reported that back-end volatility had a small impact on exhaust emissions in HD diesels. Reducing T_{90} or T_{95} raised emissions of HC and CO and lowered emissions of NO$_x$. PM emissions were not affected. They speculated that these small effects might be due to effects of volatility and molecular weight on spray patterns.

Oyama and Kakegawa [106] reported the results of Phase 1 of JCAP in which five fuels varying in T_{90} and aromatics were tested in eight truck engines. Seven were DI, three were turbocharged, one had mechanical injection and three had EGR. Engine sizes ranged from 3.6 to 21 liters. They were chosen to represent the existing Japanese truck fleet meeting 1990-1994 or 1997-1999 emission standards. The Japanese 13 mode test was used. Regression analysis showed that reducing T_{90} lowered PM emissions (~0.5 %PM/ °C T_{90}) and increased NOx emissions by a smaller amount (~0.1 %NO$_x$/ °C T_{90}).

JCAP II [107] evaluated three truck engines varying in size from 3.8 liter to 15.7 liter using the 13 mode emissions test. Three aftertreatment systems were tested – DPF, DPF + Urea-SCR, and NSR. Emission levels were targeted to be one-half the 2003 Japanese standards. When T_{90} was reduced from 335°C to 240°C, the engine with NSR catalysts had lower NO$_x$ and PM emissions by 25% and 54%, respectively.

JCAP II evaluated NO$_x$ emissions with a Urea-SCR aftertreatment system in a 13 liter engine with unit injectors and no EGR [108]. Three fuels with varying levels of T_{90} (280°C, 300°C, 330°C) were tested on the D13 emissions cycle and the JE05 transient test. Cetane was held constant, but density and T_{10} decreased as T_{90} was lowered. Results were reported in terms of T_{90}. Reducing T_{90} increased engine-out NO$_x$ emissions. It was suggested that for low T_{90} fuels, the pilot injection did not ignite, therefore causing higher heat release, higher temperatures and higher NOx formation during the main combustion event. This effect was more noticeable with the JE05 test cycle, which has lower temperatures than the D13 test cycle. At the same time, the engine-out effect was counteracted by an increase in catalyst efficiency, so that the net effect was a small decrease in NO$_x$ emissions. PM emissions decreased, and THC increased, both engine-out and tailpipe, when T_{90} was reduced.

Using the same fuel set, JCAP II [55] tested a 9 liter DI turbocharged engine having a common rail injection, EGR and a Urea-SCR/DPF aftertreatment system. Two test cycles were used – steady state D13 and transient JC05. Lowering T_{90} increased engine-out emissions of HC and decreased

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engine-out emissions of PM. Catalyst activity was too high to see an effect in the low tailpipe emissions. For NO_x, both engine-out and tailpipe emissions increased when T_{90} was lowered.

Kono et al. [119] tested three modern DI engines with high pressure injection, two of which were turbocharged. All three had EGR, one had an oxidation catalyst, and one had a complex NSR/DPF aftertreatment system. The engines were designed for 2 ton cargo trucks; one met the 1998 Japanese standards, and the other two met the 2003 standards. All were tested using the JC08 chassis-based emissions test, which involved both cold and hot start operation. Eight fuels were tested, three of which varied in T_{90} (280°C, 300°C, 330°C). Density varied as well in the fuel set, so it is not possible to unambiguously assign effects to individual properties. (These fuels appear to be the ones used in JCAP II.) No detailed analysis is presented, but the authors reported that fuel effects on NO_x were small (less than 5%). Lowering T_{90} reduced PM emissions and increased emissions of HC and CO.

Kono et al. [129] tested a Japanese 4.8 liter naturally aspirated DI engine usually used in a 2 ton truck. It was equipped with common rail injection, EGR and an oxidation catalyst. The same fuels were used as reported previously [119]. Eight different Japanese and U.S. driving cycles were used. Engine-out and tailpipe emissions were measured for all the driving cycles. Reducing T_{90} lowered PM emissions, especially engine-out. A 10°C reduction in T_{90} lowered total PM engine-out emissions between 3% and 7% in the various test cycles. Tailpipe emissions were reduced by about 3% in four of the eight cycles. SOF engine-out emissions rates were also reduced by about 5%; tailpipe SOF emissions were unaffected. Soot emissions exhibited a different response. Engine-out soot emissions were unaffected by lowering T_{90}, but tailpipe soot emissions decreased about 5%. The authors speculated that the oxidation catalyst might convert SOF into soot, so that a reduction in SOF out of the engine would translate into a reduction in soot at the tailpipe.

SUMMARY OF BACK-END EFFECTS

In LD diesels, reducing back-end volatility (lower T_{90} or T_{95}) reduced emissions of PM by a relatively small amount and did not affect HC or CO. Effects on NO_x emissions were mixed, with some evidence of an increase.

In HD diesels, reducing back-end volatility also reduced PM emissions, and increased emissions of HC and CO. For NO_x emissions, some studies showed an increase, and some showed a decrease.

D. FATTY ACID ESTERS (FAE)

Esters fit for use in diesel fuel may be made from vegetable oil or animal fat. These esters are typically made by reacting oils with an alcohol, usually methanol, in the presence of a base. The resulting esters have properties that put them in the diesel boiling range, have high cetane and contain oxygen, which may help in the combustion process. On the negative side, they have a lower energy density, and may require the use of suitable additives to counter poorer oxidative stability. A wide range of food and non-food oils may be used, such as soy, rapeseed, palm, jatropha, jojoba and pongamia. FAE made from oils are mixtures of different esters having a range of molecular weights and saturation/unsaturation levels. Full description of the chemical composition of various FAEs may be found in the literature [131].

One of the main incentives to use FAE is that they are considered renewable and generally have lower greenhouse gas equivalent emissions than petroleum-based diesel fuels. Generically, these materials are known as biodiesel. Mixtures of biodiesel and petroleum diesel are usually signified by Bxx, where xx refers to the percentage of biodiesel mixed with petroleum diesel.

ASTM has written specifications for the pure biodiesel (D 6751), and manufacturers generally certify that engines will run on fuel with up to 5% FAE, if ASTM or similar industry specifications are met.

A drawback in much research carried out to date is that tests were done with biodiesel that was splash blended into a fully formulated diesel and a number of properties changed when the biodiesel was added. Changes in emissions are due not just to the change in chemical composition, but also to

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changes in other properties such as cetane, density and boiling range. If biodiesel is used broadly, it is likely that the base fuel will be specially blended so that the entire blend meets, but does not exceed, specifications. The emissions benefits might be different in than those reported in the literature.

When evaluating the impact of FAE on PM emissions, it is important to measure each component of PM emissions. FAE may decrease carbonaceous soot, but probably does not affect sulfate emissions, and may increase the soluble organic fraction.

LIGHT DUTY DIESELS

Sirman et al. [132] tested a number of fuels in a 2.2 liter Daimler-Benz European DI, turbocharged engine with common rail injection system. No information was provided about model year or emissions certification. Emissions from a low sulfur diesel were compared to those with a mixture of 20% soy oil methyl ester (SOME) with low sulfur diesel. Emissions were measured on a 13 mode test on an engine dynamometer. With the B20 fuel, NO_x emissions increased by 3% and PM emissions were lower by 14%. Both changes were statistically significant.

Malhotra et al. [133] tested one IDI passenger car from the Indian market, with regular diesel fuel and 20% blends of Pongamia Pinnata methyl ester (PPME), Pongamia Pinnata ethyl ester (PPEE) and Jatropha Curcas methyl ester (JCME). Results for CO and PM are shown below. No data were presented for HC and NOx and no statistical analysis was provided. Results are summarized below.

	Percent Change in Emissions Relative to Diesel		
	PPME B20	PPEE B20	JCME B20
CO	- 20	- 6	- 21
PM	- 22	- 9	- 18
% SOF	- 44	- 46	- 33

Martini et al. [134] reported on tests of three biodiesels conducted for the European Commission in two 2004 model year diesel cars meeting Euro 3 emission standards. Both engines were DI, turbocharged, with EGR and oxidation catalysts. One had a common rail injection system and the other had unit injectors. Three biodiesel materials were tested: rapeseed methyl ester (RSME), a 50/50 mixture of soy methyl ester and sunflower oil methyl ester (SSME), and palm oil methyl ester (POME). RSME and SSME were tested neat, and all three were tested in a 30% mixture with two diesel base fuels.

Two petroleum diesel base fuels were tested. Diesel fuel 1 was a high quality diesel, and it was felt that the benefits of biodiesel might not be apparent. Therefore, a second base diesel, with properties closer to average was added to the program and tested in one of the cars. Diesel 2 had higher aromatics (30% vs. 20%), higher density (0.839 vs. 0.824) and lower cetane (51.5 vs. 53.5). The test matrix is shown below:

	Car 1	Car 2
Pure Biodiesel		
RSME	x	x
SSME	x	x
Diesel Fuels		
Diesel Fuel1	x	x
Diesel Fuel 2		x
30% Blends		
RSME-Diesel 1	x	x
SSME-Diesel 1	x	x
POME-Diesel 1	x	x
RSME-Diesel 2		x
SSME-Diesel 2		x
POME-Diesel		x

Results are shown below for the 30% blends:

	Percent Change in Emissions versus Base Fuel					
	30% RSME in		30% SSME in		30% POME in	
	Diesel 1	Diesel 2	Diesel 1	Diesel 2	Diesel 1	Diesel 2
Vehicle 1						
HC	+ 29		+ 37		+ 16	
CO	+ 30		+ 36		+ 3	
NO_x	+ 1		- 3		- 2	
PM	- 23		- 32		- 27	
Vehicle 2						
HC	+ 21	- 2	+ 53	+ 10	+ 6	- 11
CO	+ 36	+ 5	+ 56	+ 18	+ 22	- 6
NO_x	+ 6	+ 1	+ 2	+ 2	0	0
PM	+ 1	- 9	- 8	- 1	- 10	- 10

The three biodiesels had similar directional effects on emissions: HC, CO and NO_x emissions increased, and PM emissions decreased. POME blend seemed to have smaller impact on HC and CO, possibly because of its higher cetane number. The increases in HC and CO occurred mostly during the cold start part of the driving cycle (first 300 seconds). The impact of biodiesel on PM was different for the two cars, and the authors speculated that it might be the result of different calibration strategies for EGR and injection. Analysis of the PM emissions showed that biodiesel changed the make-up of the emissions – tending to reduce the soot fraction and to increase the SOF fraction.

The negative effects of the biodiesel blends are much smaller when Diesel 2 was used because the base fuel itself has higher emissions.

Lee et al. [4] pointed out that most of the research on oxygenates used splash blending and therefore could not decouple the changes in the other properties such as density from the addition of the oxygenate. They considered all previous conclusions tentative.

Clark et al. [135] tested a Navistar HD diesel with biodiesel, petroleum diesel and blends of the two. The feedstock oil of the biodiesel material was not disclosed. The engine was a Navistar T444E meeting 1994 U.S. emission standards, 7.3 liter displacement, turbocharged, with hydraulically actuated, electronically controlled injection system, with no EGR or aftertreatment system. The hot start portion of the HD transient FTP was used. Results are shown below for three biodiesels relative to the base petroleum diesel. Emissions of HC, CO and PM were reduced, while there was a slight increase in NO_x emissions. Changes in emissions are due to the presence of oxygen and other changes in properties, as discussed above.

	Percent Change in Emissions Relative to Diesel Fuel		
	B20	B50	B100
HC	- 4.6	- 30	- 61
CO	- 34	- 39	- 49
NO_x	+ 1.7	0	+ 4.3
PM	- 59 *	- 32	- 42
* Questionable result			

Results were compared to earlier data and shown to be consistent when considered on the basis of oxygen content.

Sharp et al, [136, 137] tested three engines with three fuels – diesel, biodiesel (Soy Oil Methyl Ester), and a 20% mixture (B20). One engine was from a highway truck, one from an urban bus, and one from a pick-up truck. The truck and bus engines had electronically controlled unit injectors and oxidation catalysts. The pickup truck engine had mechanically controlled injection. The HD transient FTP emissions test was used. Engine-out emissions of HC were reduced substantially with biodiesel, being almost eliminated for the two larger engines. Speciated results showed that the specific ozone reactivity was about the same for all fuels. Use of biodiesel substantially reduced (50-75%), but did not eliminate, the presence of PAH compounds in the exhaust. It also, as expected, increased emissions of high molecular weight oxygenated compounds. Engine-out CO emissions were cut by about 40%, and NO_x emissions increased about 10% with biodiesel. The pickup truck engine had a smaller NO_x increase and this may be related to the lower pressure injection system and how it responds to other property changes (e.g., density). Total engine-out PM emissions decreased by 25-50% due to a combination of an increase in fuel-based particulates and a larger decrease in soot. Sulfate emissions also decreased, but these were very low and only had a small contribution. B20 demonstrated the same trends as B100, but there was some indication that the benefits were somewhat higher than proportional, especially for soot. These papers did not present any statistical analysis of the results.

Wang et al. [138] tested nine trucks on a chassis dynamometer. Six were equipped with a Cummins 855 engine, with model years ranging from 1987 to 1992. This engine's displacement is 14 liters. Three trucks were equipped with a 1993/94 DDC series 60 engine, having a displacement of 11.1 liters. Two fuels were tested, a petroleum diesel and a B30 mixture, using SOME. Two driving cycles were used – the WVU (West Virginia University) truck cycle and the WVU 5 mile cycle. Both are similar and consist of a series of accelerations, cruises and decelerations. Since, in a chassis based test, the vehicle is driven to constant power output, there is no question of adjusting the engine for the lower brake specific power levels. PM emissions were 25% lower and CO emissions were 12% lower with B30. HC emissions were lower with the Cummins engine and were the same with the DDC engine. NO_x emissions

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results were different for the two engines. With the Cummins engine, B30 increased NO_x emissions, and with the DDC engine NOx emissions decreased with B30. The authors speculated that the higher NO_x emissions were the result of higher cetane, and reasoned that higher cetane results in an earlier ignition and higher temperatures and pressures. Implicit in this argument is that the two engines somehow respond to higher cetane in different, undefined ways.

McCormick et al. [139] and Graboski et al. [140] tested petroleum diesel, seven FAEs prepared from vegetable and animal oils, and 14 pure esters prepared chemically. Some were methyl esters and some were ethyl esters. All fuels were tested in a DDC Series 60 engine, with a 1991 emissions calibration. The DI turbocharged engine had a displacement of 11.1 liters. The EPA HD transient emissions test cycle was used.

Almost all esters had higher NOx and lower PM emissions than the petroleum diesel, and the methyl esters and ethyl esters had the same emissions. Because of the large numbers of chemically similar fuels that were tested, the authors were able to carry out a correlation of bulk properties for the ester fuels. They found that NO_x emissions were strongly correlated with density and cetane. Over a range of density from 0.863 g/ml to 0.895 g/ml, reducing density lowered NO_x emissions by about 25%. Increasing cetane from 42 to 77 lowered NO_x by about 20%. Neither density nor cetane affected PM emissions for these fuels. Since the molecular weights of these fuels varied as well, the volatility properties changed, although it was not reported. These data suggest that oxygen is the driving variable for the effect of biodiesel on PM emissions, but that oxygen alone does not explain the increase in NOx emissions relative to petroleum diesel.

McCormick et al. [141] tested a number of fuels in order to develop a strategy to mitigate the increase in NOx emissions seen with use of biodiesel or biodiesel blends. They tested two biodiesel materials, esters of yellow grease and soy oil, along with Fischer Tropsch diesel, cetane improvers and low aromatics diesel. The engine was a 1991 calibration DDC Series 60 11.1 liter turbocharged DI engine tested over the HD transient FTP test. For B20 fuel, the increase in NO_x emissions could be mitigated or reversed by adding 46% Fischer Tropsch diesel, reducing aromatics from 30% to 10%, or by adding cetane improvers to raise cetane about 0.5 CN. No statistical analysis was presented.

Xiaoming et al. [142] tested emissions from two engines with two base diesels and two biodiesel blends, B20 and B50. The engines, presumably Chinese models, were 11.9 and 5.8 liter turbocharged DI engines, with no information about their emissions control. The Chinese 13 mode steady state test was used to measure emissions. B20 was tested in the larger engine and B50 was tested in the smaller engine. Responses are shown below. PM and CO responses were similar, while there were differences in size for NO_x and in direction for HC. No statistical analysis was presented to evaluate the results.

	Percent Change in Emissions Relative to Diesel Fuel	
	B20/Engine A	B50/Engine B
HC	+ 7	- 29
CO	- 8	- 11
NO_x	+ 6.8	+ 27
PM	- 13	- 12

JCAP [55] measured PM numbers and size distribution in a 9 liter turbocharged engine with EGR and Urea-SCR aftertreatment. The engine met 2005 emission standards. B5 (5% RSME) was compared to a base diesel, and no obvious effects were seen in particle number or size distribution over the transient JE05 test. The focus of this portion of JCAP was not fuel effects, but aftertreatment effects, so the conclusions are based on limited testing and may not be generally applicable.

In 2002, EPA prepared an analysis of the effect of biodiesel on diesel emissions [91] and concluded that for HD diesels, biodiesel reduced emissions of HC, CO and PM and increased emissions of NOx. The increase in NO_x emissions was much less than the decrease in the other emission components. Not enough data were available to draw any conclusions about LD diesels.

Based on the data reviewed here, the conclusions presented by EPA are still valid, and would seem to apply to LD diesels as well. PM reductions are generally seen in the soot component, while emissions of the SOF component may tend to increase. There is good evidence that biodiesel reduces PM emissions because of its oxygen content, and that the increase in NO_x emissions may be the result of biodiesel's impact on properties such as cetane and density.

No data were found that examined FAE impacts in the presence of catalytic aftertreatment systems. Neither were data found that tested fully formulated fuels, not splash blended mixtures.

E. OTHER OXYGENATES

A number of other oxygenates have been evaluated in diesel fuel. These include ethers, carbonates, and methoxy compounds. One class of methoxy compounds tested is glymes. Mono-glyme is 1,2 dimethoxyethane, also known as dimethyl glycol or ethylene glycol dimethyl ether. Di-glyme, tri-glyme and tetra-glyme are similar compounds with additional dimethyl ether linkages in the backbone of the molecule.

Tsurutani et al. [102] tested nine oxygenates in a Toyota Corolla with a naturally aspirated 2 liter engine, with EGR but no catalyst. The fuels included blends (10%-25%) of mono- di- tri- and tetra-glymes, ethers, heavy alcohols and esters. Tests were conducted over the Japanese 10.15 and European NEDC cycles. Reductions of PM were measured and there was a strong correlation with oxygen content only. Based on tests with 20% di-glyme, the impact on PM emissions was primarily a reduction in soot emissions; SOF was not affected. There was little if any impact on NOx emissions.

Beatrice et al. [143] tested 10%, 20% and 30% di-glyme in a relatively clean Finnish summer diesel. The engine was a 1.9 liter Fiat M724 DI diesel with electronic EGR, common rail injection and an oxidation catalyst. Five steady state modes were chosen to approximate the full transient cycle. Reductions were observed for HC, CO and soot for all conditions. This was attributed to a higher rate of combustion with the oxygenated blends. NOx results were somewhat scattered, with reductions seen in 2 modes, and increases seen in three modes. The authors argued that higher cetane number of the blends may have contributed to the effects measured here.

Hess et al. [144] tested a mixture of 20% mono-glyme/80% di-glyme, blended at 5%, 10% and 15% in a U.S. diesel fuel. A 1.9 liter VW DI, turbocharged engine was tested at six steady state conditions. PM emissions decreased with increasing oxygenate content, while HC and NOx emissions were generally unaffected. Surprisingly, CO emissions tended to increase with increasing oxygen content. The authors argued that oxygenates provide additional oxygen in the rich premix zone and this tends to form additional CO. The additional CO reduces the concentration of soot precursors, primarily low molecular weight olefins.

As part of the Ad Hoc Fuel Group of the PNGV program, Szymkowicz et al. [145] tested 15% mono-glyme in a low sulfur diesel fuel, with a prototype 1.3 liter DI turbocharged engine with common rail injection and EGR. Six steady state modes were tested and results reported for a weighted average to approximate FTP conditions. Mono-glyme reduced PM emissions by about 30%, mostly as dry PM (non-volatile) and had little or no impact on NO_x. HC and CO were not reported.

Hilden et al. [146] tested a number of oxygenates, shown below, in a low sulfur diesel fuel. These represented a range of volatilities and two different classes (aromatic and aliphatic).

Compound	Acronym	Percent Oxygen in Molecule	Percent Oxygen in Tested Blend
Dipropylene glycol monomethyl ether	DPGME	32%	6%
Tripropylene glycol monomethyl ether	TPGME	32%	L: 3.5% H: 6.5%
Di-isobutyl adipate	DIIBA	25%	6.3%
Di-isobutyl phthalate	DIBP	23%	6%

The test engine was a 1.3 liter DI engine with common rail injection. Four steady state test mode were used. Only NOx and PM were reported. Results are shown below for the standard EGR configuration.

Fuel	Percent Change in Emissions	
	NO_x	PM
DPGME	+ 3.2	- 23
TPGME-L	- 6.3	- 4.5 (NS)
TPGME-H	+ 1.5 (NS)	- 18.2
DIIBA	- 0.5 (NS)	- 27
DIBP	+ 8.1	+ 16

The oxygenates reduced PM emissions, with the exception of the aromatic DIBP. The increase with DIBP was the result of higher levels of volatile PM, probably because of the aromatic nature of the molecule. There were no differences in particle size distribution among the oxygenates. NO_x emission effects were small and somewhat variable. The authors suggested that the large reductions in PM could be used to increase the EGR rate and thereby optimize both emissions components.

Ball et al. [147] tested dimethoxymethane (DMM) blended at 15% into a low sulfur diesel, in a DaimlerChrysler 2.2 liter DI engine with common rail injection and closed-loop, variable EGR. Four steady state modes were used, and results are provided for the weighted mass emissions, shown below

	Percent Change in Emissions
HC	- 14 (NS)
CO	- 4.4 (NS)
NO_x	+ 18
PM	- 36
PM-SOF	- 23

Adding DMM reduced PM, mostly through reductions in SOF, increased emissions of NO_x and had no statistically significant effect on HC or CO. Emissions of individual compounds such as PAH were generally lower but not statistically significant, with the exception of gas phase benzene.

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JCAP II [107] tested 10% di-glyme (3.8% oxygen) in two different base fuels in a 2000 model year car having a 2.5 liter engine, with EGR, and a catalyzed DPF aftertreatment. NO_x emissions were higher with the oxygenate for both base fuels. PM results were mixed. In both cases, the effects were less than 10%, and assumed to be not statistically significant. The small size of the PM effect may be due to the presence of the DPF.

Kozak et al. [148] tested six oxygenates at 5% blends in a Euro 5 diesel (9 ppm sulfur). Shown below, the compounds varied in molecular weight and density. One vehicle was tested – a 1.3 liter DI turbocharged engine with common rail injection, closed-loop EGR and an oxidation catalyst. The vehicle met Euro 4 emission standards. The European driving cycle (NEDC) was used for the tests.

Compound	Percent Oxygen in Tested Blend
Mono-glyme	1.85
Di-glyme	2.02
Tri-glyme	2.12
Tetra-glyme	2.16
Diethylene glycol dibutyl ether	1.17
Dipropylene glycol dimethyl ether	1.60

During the cold start portion of the cycle (UDC), when HC and CO emissions are high, the presence of the oxygenates tended to reduce HC and CO emissions by about 20%. Results for NOx and PM were about the same for both phases of the test cycle. NOx emissions increase between 2% and 7%, while PM emissions were reduced between 8% and 13%. There was no obvious correlation between oxygen content and emissions effects, possibly because of changes in other properties such as volatility and density.

HEAVY DUTY DIESELS

Cheng and Dibble [149] tested DMM and diethyl ether (DEE) in concentrations up to 30% in a petroleum diesel. A 1993 model year 5.9 liter DI turbocharged Cummins B Series engine was tested at nine steady state modes chosen to cover a wide range of the operating map. Results are shown below for the 10% and 30% cases. While there were variations across the modes, adding these oxygenates generally increased HC and CO emissions, and lowered NO_x and PM emissions. The authors speculated that high concentrations of these oxygenates may have poor combustibility, may affect the injection spray pattern, or may cause the injectors to weep liquid fuel. No statistics were reported for these results.

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	Percent Change in Emissions Relative to Diesel Fuel			
	DMM		DEE	
	10% Blend	30% Blend	10% Blend	30% Blend
HC	+ 38	+ 50	+ 30	+ 119
CO	+ 2	+ 31	+ 2	+ 26
NO_x	- 7	- 10	- 1	- 9
PM	- 14	- 35	- 13	- 14

Chapman et al. [150] compared diesel fuel with a 5.6% splash blended mixture of CETANER™ (2% oxygen) in a HD Navistar 7.3 liter DI turbocharged engine hydraulically activated, electronically controlled unit injectors. CETANER™ is a 20/80 mixture of mono-glyme and di-glyme. Eight steady state test modes were chosen to approximate the transient FTP emissions test cycle. Using weighted averages of the eight mode test, HC and NO_x emissions were reduced by 6% and 5.4%, respectively. CO emissions were unchanged. PM emissions appear to be reduced, but weighted averages were not reported. No statistical analysis was presented.

Vertin et al. [151] tested DMM at a number of different splash blended concentrations with a 1993 model year Cummins B Series 5.9 liter DI turbocharged engine with mechanically controlled fuel injection. Nine steady state modes were chosen to cover a variety of operating conditions. Shown below are comparisons of 10% and 30% DMM versus the diesel base. These are in surprisingly good agreement with the results reported above by Cheng and Dibble.

	Percent Change in Emissions Diesel Fuel → DMM	
	10% Blend	30% Blend
HC	+ 36	+ 73
CO	+ 1	+ 60
NO_x	- 7	- 10
PM	- 14	- 35

SUMMARY OF OTHER OXYGENATES

Considering the large number of oxygenate compounds that may be used in diesel fuel, there is not a lot of data on their emission effects. There is contradictory data and some results do not agree with data collected on fatty acid esters. If the impacts on emissions were caused by the presence of oxygen, we would expect the results to be similar. While PM emissions are generally lower, HC, CO and NO_x results are mixed. In LD diesels, HC and CO emissions tend to be lower and NO_x emissions tend to be higher. In HD diesels, HC and CO emissions tend to be higher and NO_x emissions tend to be lower. The reason for these differences is not clear.

If these compounds will be seriously considered for commercial use, more and better data should be obtained.

F. FISHER TROPSCH FUELS

The Fischer Tropsch (FT) process is a high temperature catalytic process that reacts CO and H_2 to produce a mixture of HC. The specific compounds generated are dependent on reactor design,

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reaction temperature and pressure, and catalyst composition. Production of the feed stream is usually from natural gas, but may also be from petroleum or coal. In some references, FT is referred to as GTL (gas-to-liquids). Another blendstock with similar properties is HVO (hydrogenated vegetable oil), and it will be discussed in this section.

Today, FT products are usually in the diesel boiling range although lighter, naphtha products and lubricant basestocks can be made as well. Most FT diesel products require some sort of upgrading to improve quality. This includes creating iso-paraffins from normal paraffins and/or removing waxy materials to improve cold flow properties.

FT fuels usually have extremely high cetane, almost no aromatics and essentially zero sulfur, and these properties clearly impact exhaust emissions. FT diesel also has lower volumetric energy density than petroleum diesel and, therefore, fuel economy and peak power are lower. Lubricity of FT diesel is poorer than petroleum diesel, and, if used by itself, additives to improve lubricity will probably be required.

When discussing the literature on FT products, it is important to specify the composition of the petroleum diesel against which FT is being compared. Aside from other issues such as model to model differences in response, this is probably a major contributor to the different results seen in the literature. As with oxygenates, a major limitation in the literature is that most studies were conducted with splash blended mixtures of petroleum diesel and FT product, making it difficult to determine the reason for the emissions effects.

A number of important questions concern the effects of FT diesel, and its ultimate use in the fuel pool.

- Are the effects of FT due to its properties alone? Most studies did not evaluate this question.
- Are the effects linear?
- How should it be used in practice - alone or in blends? If alone, will this require specials engines or special distribution networks? If in blends, will overall fuel quality remain the same or will it improve?

Unfortunately, much of the research reported in the literature does not help answer these questions.

LIGHT DUTY DIESELS

Payri et al. [152] tested Sasol FT diesel along with a standard diesel in two samples of a PSA diesel car with a 2.0 liter DI turbocharged engine with common rail injection meeting Euro 2 standards. A summary of fuel properties is shown below:

Fuel Property	Units	Diesel	FT
Density, @15°C	g/ml	838	770
Viscosity	mm^2/s	2.5	2.1
Cetane Number		51.4	73
H/C ratio		1.85	2.15
Heat of Combustion	MJ/kg	43.1	43.5

Results for the two cars are very similar as shown below:

	Percent Change in Emissions Diesel → FT	
	Car 1	Car 2
HC	- 58%	- 56%
CO	- 62%	- 51%
NO$_x$	- 5%	+ 3%
PM	- 25%	- 41%

Payri et al. concluded that an engine could be modified or redesigned to take advantage of the properties of FT fuels. An example would be to increase the use of EGR while still maintaining PM emissions at an acceptable level.

Sirman et al. [132] tested a number of fuels in a 2.2 liter Daimler-Benz European DI, turbocharged engine with common rail injection system. No information was provided about model year or emissions certification. A sample of Shell SMDS FT diesel was tested along with a 20% blend in low sulfur, low aromatics diesel and the low sulfur diesel base fuel. The main property differences were cetane (84 vs. 67), density (0.781 vs. 0.811) and T$_{90}$ (325°C vs. 261°C). Emissions results are summarized below. Emissions changes were consistent with the property changes, except for the results with FT20 for HC, which increased relatively to the base fuel.

	Percent Change in Emissions Relative to diesel base fuel	
	FT20	FT
HC	+ 28%	0
CO	- 11%	- 14%
NO$_x$	- 3%	- 3%
PM	- 7%	- 19%

Szymkowicz et al. [145] tested a FT diesel, an ARB diesel and a low sulfur diesel in a prototype 1.3 liter DI turbocharged engine with common rail injection and EGR. Two levels of EGR were tested, conventional and maximum. Six steady state modes were tested and results reported for a weighted average to approximate FTP conditions. Compared to the low sulfur diesel, the FT diesel had higher cetane (81 vs. 65), lower specific gravity (0.780 vs. 0.817) and lower aromatics (1.2% vs. 8.9%). Results are shown below for the comparison to the low sulfur diesel:

	Percent Change in Emissions LSD → FT	
	Conventional EGR	Maximum EGR
Total PM	- 37%	- 32%
NO$_x$	- 8%	- 2%

Johnson et al. [153] tested a pure FT diesel, various cuts of the FT diesel, and blends with petroleum diesel fuels in a Peugeot 405 LD diesel car. Fuel property differences are shown below:

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Fuel Property	Units	UK Diesel	FT
Density	g/ml	0.851	0.775
Cetane Number		51.1	79
Aromatics	%	29.2	0
Sulfur	ppm	1400	0

Over the European emissions cycle, all components of the emissions were reduced: HC by 73%, CO by 54%, NO_x by 4% and PM by 63%. Different boiling range cuts were prepared and tested, and there were no differences in their emissions behavior, suggesting that the heavy paraffinic molecules present in FT diesel are not as detrimental to emissions as the heavy molecules present in petroleum diesel. The FT diesel was blended with other refinery streams to produce a diesel with similar properties to a petroleum diesel. Emissions tests showed that both fuels had similar levels of emissions, suggesting that it is the measureable typical properties of the FT material that contribute to its emissions performance. Equations developed in the EPEFE program were applied to the emissions data reported in this paper and they did a poor job of predicting the performance of the FT fuels. The authors suggested that the poor performance was a result of the fuels being outside the range of properties over which the equations were developed. However, testing this type of predictive equation on the data from one vehicle is not an appropriate test, considering the typically wide range of responses measured in the vehicle fleet.

Schubert et al. [154] tested a Syntroleum produced FT diesel and a petroleum diesel in a 1999 model year Volkswagen Golf with a 1.9 liter, DI engine. Major properties of the fuels are summarized below. Emissions tests were carried out using the FTP, US06 and HWFET cycles.

Fuel Property	Units	Diesel	FT
Specific Gravity		0.8455	0.7716
Cetane Number		46.7	73.6
Aromatics	wt. %	31	0.7
Sulfur	ppm	300	< 10

For the FTP cycle with FT, THC and PM emissions were lower by 25% and NO_x emissions were 12% higher. CO emissions were too low to quantify any differences. Toxics emissions with FT were 34% less than with the petroleum diesel. Particle size distribution was similar for both fuels.

Schaberg et al. [155] compared a petroleum diesel with a FT diesel produced by Sasol. Fuel properties are shown below.

Fuel Property	Units	Diesel	FT
Specific Gravity		0.8705	0.7647
Cetane Number		41.5	74.8
Aromatics	%	38.4	< 1
Sulfur	ppm	404	< 1

A 1.9 liter turbocharged VW passenger car engine was tested, and emissions were measured over 5 steady state test modes. On average, NO_x emissions increased by 6% and PM emissions decreased by 50%. Both the soot and volatile fraction of PM were reduced. The smaller numbers of nanoparticles were assumed to result from the lack of sulfur available to form nucleation mode particles. Changes in HC and CO, while large on a percentage basis, were not statistically significant.

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Myburgh et al. [156] tested a FT diesel produced by Sasol and two Japanese petroleum diesels in an SUV complying with Japanese 1998 emission standards. The engine was 3.0 liter turbocharged diesel with variable EGR, common rail injection and an oxidation catalyst. Properties of the fuels are:

Fuel Property	Units	FT Diesel	Low S Diesel	Market Diesel
Density	g/ml	0.768	0.818	0.832
Cetane Number		74.1	57.5	58
Aromatics	wt. %	0.1	21.2	24.4
Sulfur	ppm	< 1	29	410

Emissions of HC and CO were too low to see any differences among the fuels, and there were no differences in NO_x emissions. PM emissions with the FT diesel were 29% below the low sulfur diesel and 62% below the market diesel.

Nishiumi et al. [130] tested four FT fuels and one petroleum diesel that met Euro 4 standards. Two properties were varied by adjusting a full boiling FT diesel – cetane number and boiling range. Properties are shown below:

Fuel Property	Units	FT A	FT B	FT C	FT C	Diesel
Boiling Range (T_{10}-T_{90})	°C	225-328	236-252	221-329	238-254	223-327
Cetane Number		85	85	52	53	52
Density	g/ml	0.7733	0.7671	0.7865	0.7825	0.8295
Aromatics	%	0.3	0.5	0.1	0.0	15.6
Sulfur	ppm	< 1	< 1	< 1	< 1	9

FT A was the full boiling range FT fuel, and it was adjusted by changing the normal/isoparaffin ratio, and/or by cutting out the heavy fractions. The test vehicle was a Toyota Avensis with a 2.0 liter, DI turbocharged engine with common rail injection and cooled EGR. Engine calibrations were not adjusted to take advantage of fuel properties such as high cetane. The European driving cycle was used for emissions tests. Comparisons of the fuels to the petroleum diesel are shown below:

Percent Change from Diesel				
Fuel	FT A	FT B	FT C	FT C
CN/Boiling Range	H/W	H/N	L/W	L/N
PM	- 25%	- 43%	- 40%	- 55%
NO_x	+ 13%	+ 20%	- 5%	0
THC	- 45%	- 35%	+ 35%	+ 30%

In this engine, low cetane helped promote reductions in PM while not increasing NO_x and while allowing THC to increase. The narrow boiling range seemed to provide somewhat better performance with respect to PM emissions. From an analysis of the fuels and the SOF of the particulates, the authors concluded that molecules with carbon number greater than 18 are major contributors to PM SOF.

Schaberg et al. [157] carried out tests using the same engine in a car and mounted on a dynamometer. The engine was a 2003 model year, Mercedes Benz 2.2 liter turbocharged engine with common rail injection, EGR and two oxidation catalysts, meeting Euro 3 emission standards. The European emissions test cycle was used. Four fuels were tested – a low sulfur diesel, Sasol FT diesel, a 50/50 mixture and an 80 Diesel/20 FT mixture. Properties of the fuels are shown below:

Fuel Property	Units	Diesel	FT
Density	g/ml	0.836	0.768
Cetane Number		54	74
Aromatics	%	26.8	0.1
Sulfur	ppm	7	< 1
T_{95}	°C	354	321

HC and CO emissions were reduced by more than 90% with FT diesel compared to petroleum diesel. This was ascribed to the operation of the oxidation catalyst which absorbs HC and CO during cold start and then oxidizes them after operating temperatures are reached. Engine-out emissions are low enough that there is no breakthrough during cold start with FT diesel. With petroleum diesel, engine-out emissions are greater than the storage capacity of the catalysts and emissions break through to the tailpipe.

NOx emissions were about the same for all the fuels. PM emissions were reduced about 30% with FT diesel. When the 50/50 mixture was tested, the reduction was 22%, slightly more than a linear interpolation would predict. A large part of the PM benefit was seen in soot emissions.

By adjusting engine operating parameters, particularly EGR, it was estimated that much lower NOx emissions could be achieved (35% reduction) while still maintaining the low PM emissions seen in the baseline tests.

Kitano et al. [158] tested a passenger car with 2.0 liter DI turbocharged engine, with EGR and Toyota's DNPR (Diesel Particulate NO$_x$ Reduction) system, an oxidation catalyst, and sensors to control A/F ratio and exhaust temperature. Five fuels were tested in the car. Two sets of two fuels each were based on two different Shell FT base fuels differing in volatility, and the fifth fuel was a petroleum diesel meeting Euro 4 standards. Properties are shown below:

Fuel Property	Units	FT-J2	FT-J3	FT-N2	FT-N3	Diesel
Boiling Range (T_{10}-T_{90})	°C	227 - 284	258 - 344	173 - 247	181 - 306	206 - 328
Cetane Number		85	85	71.5	71.5	53.4
Density	g/ml	0.773	0.786	0.751	0.764	0.840
Aromatics	%	< 0.1	< 0.1	< 0.1	< 0.1	18.9
Sulfur	ppm	< 1	< 1	< 1	< 1	33

Vehicle emission tests were carried out with and without the DPNR system. In the absence of DPNR, HC and CO emissions were reduced by more than 60% and NOx emissions increased about 5%. There were no major differences among the FT fuels. PM emissions were reduced between 30% and 70%, depending on the FT fuel. The reasons for the differences are probably related to the distillation

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differences, with lower T_{90} and narrower distillation improving atomization and dispersion, and leading to faster evaporation, all of which improves combustion performance and lowers PM emissions.

With the DPNR in operation, there were no differences among any of the fuels for NOx and PM emissions. It is possible that the effectiveness of the catalyst for PM reduction is so high, that small differences cannot be measured.

An interesting experiment showed that there seemed to be a sulfur effect on NOx efficiency even with the "zero" sulfur FT fuels. The authors attribute this effect to sulfur from the lubricant.

Clark et al. [159] tested six cars in two phases to model use of FT material in the short term in developing countries, and in the longer term in developed countries. In Phase 1, they tested three cars meeting Euro 2/3 emission standards (1996-1999 model years) with GTL blends (15%, 30%, 50%) in two regular sulfur base fuels (500 ppm, 1000 ppm). Average results are shown below, along with an extrapolated estimate of pure GTL diesel.

	Average Percent Change in Emissions Relative to Base Diesel			
	15% FT	30% FT	50% FT	100% FT (Est.)
HC	- 41	- 57	- 68	- 80
CO	- 26	- 41	- 52	- 67
NO$_x$	+ 0.6	- 0.3	- 2.3	- 9.8
PM	- 33	- 41	- 50	- 64

In Phase 2, three model year 2003 cars, certified to Euro 4 standards were tested with GTL blends (15%, 30%, 50%, 100%) in a low sulfur (40 ppm), higher cetane (54 CN) petroleum diesel. No data was provided about aftertreatment systems in these cars. Results in this phase were much more variable. HC and CO emissions were consistent across the vehicles and consistent with the Phase 1 results. For 100% FT, HC benefits averaged 49% and CO benefits averaged 81%. PM differences ranged from a benefit of 33% to an increase of 14%. NO$_x$ emissions ranged from a benefit of 6% to an increase of 18%. The authors speculated that this behavior may be the result of the interaction of the FT fuel with engine control systems such as EGR. With lower density fuels such as FT, EGR rates tend to decrease.

Kitano et al. [160] tested two FT diesels along with a petroleum ultra low sulfur Euro 4 diesel. Properties are shown below. An interesting feature of this program is that the base diesel fuel had essentially zero sulfur, so it is a little easier to assign reasons for any emissions differences seen.

Fuel Property	Units	FT-A	FT-B	Diesel
Boiling Range (T_{10}-T_{90})	°C	249 - 339	174 - 247	224 - 330
Cetane Number		85.2	71.5	52.7
Density	g/ml	0.7852	0.7510	0.8340
Aromatics	Vol. %	< 0.1	< 0.1	19.3
Sulfur	ppm	< 1	< 1	5

The program used a 2.0 liter DI turbocharged engine with common rail injection in a car and on an engine dynamometer. The car was tested with and without a DNPR aftertreatment system, using the European NEDC test cycle. FT did not affect NO$_x$ emissions, with or without aftertreatment. PM emissions were lower with FT without aftertreatment. FT-B, which had low T_{90}, had lower PM emissions

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than FT-A. With the DPNR system in place, PM emissions were so low that differences among the fuels could not be discerned. HC and CO emissions were lower with FT in both configurations.

One problem noticed with the more volatile FT diesel (FT-B) occurred when it was injected into the exhaust to help reduce NO$_x$ emissions. It appeared to vaporize rapidly and did not combust properly. The authors speculated that engine operations could be optimized for FT properties so that emissions could be reduced without the usual degradation in fuel economy.

HEAVY DUTY DIESELS

Norton et al. [161] tested emissions from four Class 8 trucks powered with 1996/97 model year Caterpillar 3176B 10.3 liter DI turbocharged engines. All trucks were tested on Shell FT diesel and a California diesel, shown below:

Fuel Property	Units	CA Diesel	FT
Density, @15°C	g/ml	0.8337	0.7845
Cetane Number		54	> 74
Aromatics	wt. %	18.1	0.3
Sulfur	ppm	100	< 5

Testing was over a five mile driving course on a chassis dynamometer. Average results for the four trucks are shown below. All components of emissions were reduced, although no statistics were provided describing the significance of the results. No driving performance difference between the fuels was reported.

	Percent Change in Emissions Diesel → FT
HC	- 40%
CO	- 18%
NO$_x$	- 12%
PM	- 24%

Clark et al. [135] tested a Navistar HD diesel with two different FT diesels and with two petroleum diesels. Properties of the fuels are shown below. It is interesting to note that FT 1 had a relatively high sulfur level. The engine was a Navistar T444E meeting 1994 U.S. emission standards. It was a 7.3 liter turbocharged engine with hydraulically actuated, electronically controlled injection system, and no EGR or aftertreatment system. The hot start portion of the HD transient FTP was used.

Fuel Property	Units	US Diesel	CA –Diesel	FT 1	FT 2
Density, @15°C	g/ml	0.85	0.8329	0.7905	0.8007
Cetane Number		44	54	74	51
Aromatics	wt. %	< 30	18	0.1	10
Sulfur	ppm	3500	100	< 500	< 10

Results are shown below for the fuels. Emissions of all four regulated components HC, CO, NOx and PM were reduced. The differences between the two FT samples bracket the reduction seen with the

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CA diesel, and this is a reflection of the properties of the fuels. The reduction on PM seems small compared to other reports of similar fuels.

	Percent Change in Emissions Relative to US Diesel		
	CA Diesel	FT 1	FT 2
HC	- 21	- 43	- 9
CO	- 31	- 39	- 13
NO_x	- 9	- 14	- 6
PM	- 9	- 14	- 15

Atkinson et al. [162] tested the same Navistar engine reported by Clark et al. [135] with two fuels, a FT diesel and a typical U.S. diesel, shown below.

Fuel Property	Units	US Diesel	FT
Specific Gravity		0.838	0.7845
Cetane Number		48.7	73.7
Aromatics	wt. %	24.7	0.1
Sulfur	ppm	< 3500	< 500

Emissions were measured at twelve steady state modes to span a wide range of engine performance. Considering the average of all test conditions, the FT fuel reduced all emission components, HC by 14%, CO by 21%, NO_x by 20% and PM by 31%. No statistical analysis was presented.

The authors present an interesting discussion of the reasons for some of the emission effects. The FT fuel, because of its higher cetane, had a shorter ignition delay by about 10 degrees, which reduced evaporation before ignition leading to a more consistent heat release shape. The FT fuel also had a longer burn duration, even after considering the early ignition. These combine to create a lower peak pressure for the FT fuel and therefore lower NO_x emissions. While these explanations may be accurate for this particular engine technology, other technologies may have different operating maps, and newer technologies may adjust operating conditions such as injection timing/duration and EGR operation to compensate for differences in fuel properties. Therefore, it is necessary to test a variety of engines and technologies.

Norton et al. [161] tested a petroleum diesel, a synthetic diesel made by Mossgas, and a 50/50 mixture. Properties are shown below. The synthetic diesel is made from natural gas through a FT reaction that first produces olefins. It differs from typical FT diesel in that it has a significant aromatics concentration, and a cetane number that is in the petroleum diesel range.

Fuel Property	Units	US Diesel	Mossgas FT
Density	g/ml	0.838	0.8042
Cetane Number		48.7	48.9
Aromatics	wt. %	25	9
Sulfur	ppm	200	< 5

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Six urban buses with DDC6V92 2-stroke, DI turbocharged 9 liter engines were tested. Three of the buses had rebuilt engines and retrofitted oxidation catalysts. The buses were tested on chassis dynamometer using the Central Business District driving cycle (SAE J1376).

Average changes from the petroleum diesel are shown below. The synthetic diesel reduced emissions of all components. For the 100% synthetic diesel, HC, NOx and PM reductions were similar for the two engines groups, and CO effects were different. The 50/50 mixture seemed to give a little more than half the benefit of pure synthetic diesel, especially in the rebuilt and retrofitted engines. No statistical analysis was provided to assess the significance of the results.

	Percent Change in Emissions Relative to US Diesel			
	Synthetic Diesel		50/50 Mixture	
	Old Engines	Retrofitted Engines	Old Engines	Retrofitted Engines
HC	- 20	- 35	- 7	- 20
CO	- 26	- 49	- 7	- 26
NO$_x$	- 5	- 8	- 5	- 5
PM	- 20	- 31	- 6	- 20

Cheng and Dibble [149] tested a petroleum diesel and a FT fuel made at Shell's Malaysia plant. A model year 1993 5.9 liter DI turbocharged Cummins B Series engine was tested at nine steady state modes chosen to cover a wide range of the operating map.

Fuel Property	Units	US Diesel	Shell FT
Density	g/ml	0.8473	0.7837
Cetane Number		49.1	> 74
Aromatics	wt. %	16	0.3
Sulfur	ppm	98	< 5

Results are shown below comparing the FT diesel with the petroleum diesel. There were large reductions in all emissions components, similar to reduction seen in other programs.

	Percent Change in Emissions Diesel → FT
HC	- 45
CO	- 42
NO$_x$	- 9
PM	- 28

Schaberg et al. [163] tested two petroleum diesels (U.S. and ARB), a Sasol FT diesel, and two mixtures (30 Sasol/70 US and 50 Sasol/50 US). Fuels properties are shown below.

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Fuel Property	Units	US LSD	ARB Diesel	Sasol FT
Density	g/ml	0.8450	0.8432	0.7698
Cetane Number		46.2	52.6	> 74.8
Aromatics	wt. %	24.5	9.5	0.7
Sulfur	ppm	300	130	< 5

The engine used in this program was a 1999 model year DDC Series 60, 12.7 liter DI turbocharged engine electronically controlled unit injectors. Both cold start and hot start tests were run according to the U.S. transient FTP cycle.

Results are shown below for cold and hot cycles. Emissions of all the exhaust components were lower for both cycles. Most of the reduction in PM was the result of lower emissions of soot or carbonaceous particles. This is probably the result of higher H/C ratio because of the low aromatic levels in FT fuels. Sulfate emissions were also lower, tracking the fuel sulfur levels, but these were a relatively small fraction of the total PM. Detailed statistics were not reported for these data.

	Percent Change in Emissions Relative to US Low Sulfur Diesel							
	Hot Start				Cold Start			
	ARB Diesel	Sasol FT	S30	S50	ARB Diesel	Sasol FT	S30	S50
HC	- 23	- 37	- 34	- 33	- 26	- 63	- 46	- 46
CO	- 6	- 37	- 23	- 22	- 12	- 47	- 17	- 31
NO$_x$	- 7	- 17	- 3	- 10	- 15	- 23	- 8	- 18
PM Total	- 7	- 37	- 18	- 9	- 15	- 46	- 19	- 19
Soot	- 2	- 49	- 23	- 7	- 16	- 48	- 41	- 14
VOF	- 10	- 10	- 7	- 8	- 14	- 41	+ 11	- 24

Johnson et al. [153] tested three fuels – FT diesel, U.S. low sulfur diesel and ARB diesel in a 1991 DDC Series 60 11.1 liter DI turbocharged engine with electronically controlled injection. Properties of the fuels are shown below:

Fuel Property	Units	US Diesel	ARB Diesel	FT
Density	g/ml	0.845	0.842	0.774
Cetane Number	—	45.5	50.2	74
Aromatics	wt. %	31.9	8.7	0.26
Sulfur	ppm	300	300	0

Emissions are shown below relative to the U.S. low sulfur diesel:

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	Percent Change in Emissions Relative to US LSD	
	ARB	FT
HC	- 22	- 41
CO	- 16	- 45
NO$_x$	- 4	- 9
PM	- 10	- 32

Johnson et al. argue that a good use of FT diesel would be as a blendstock, and bring a number of examples to show how poorer quality refinery blendstocks could be used in combination with FT diesel and still achieve low emissions, while potentially increasing the available volume of diesel fuel.

Fanick et al. [164] tested two diesel engines and four diesel fuels. One was a 1999 model year 5.6 liter Cummins B Series DI turbocharged engine tested on a dynamometer and the other was a similar engine tested in a 2000 model year heavy LD pickup truck. The engine was tested using the EPA transient HD test cycle, and the pickup was tested using the FTP, HFET and US06 cycles.

Properties of the four fuels are shown below:

Fuel Property	Units	US Diesel	ARB Diesel	Swedish Diesel	FT
Density	g/ml	0.8455	0.8341	0.8194	0.7716
Cetane Number		46.7	51.4	52.4	73.6
Aromatics	wt. %	30.7	8.1	3.7	0.7
Sulfur	ppm	300	155	< 10	< 10

Results from the HD transient test and the FTP are shown below:

	Percent Change in Emissions Relative to US Diesel					
	HD Transient			FTP		
	ARB Diesel	Swedish Diesel	FT Diesel	ARB Diesel	Swedish Diesel	FT Diesel
HC	- 16	+ 3	- 41	- 11	- 15	- 30
CO	- 15	- 13	- 30	- 11	- 14	- 50
NO$_x$	- 8	- 11	- 20	- 11	- 14	- 23
PM	- 18	- 27	- 40	- 11	- 27	- 33
Toxics	- 25	- 9	- 34	- 8	- 5	- 32

Changes in emissions due to fuels were similar for the HD transient and the FTP. For the more aggressive driving cycles (HFET and US06), the fuel effects on HC and toxics were smaller and the effects on PM were larger. No statistical analysis was reported.

McCormick et al. [141] tested a number of fuels in order to develop a strategy to mitigate the increase in NOx emissions seen with use of biodiesel or biodiesel blends. Properties of the base diesel and FT diesel are shown below.

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Fuel Property	Units	US Diesel	FT
Specific Gravity		0.8476	0.7845
Cetane Number		47.4	> 74.8
Aromatics	vol. %	31.9	*
Sulfur	ppm	430	< 10
* Aromatics not reported, assumed to be extremely low.			

The engine was a 1991 calibration DDC Series 60 11.1 liter turbocharged DI engine tested with the HD transient FTP. Relative to the petroleum diesel, FT diesel reduced emissions of HC by 65%, CO by 24%, NOx by 15% and PM by 34%. For B20 fuel, the increase in NOx emissions could be mitigated or reversed by adding 46% FT diesel. No statistical analysis was presented.

Schaberg et al. [155] compared a petroleum diesel with a FT diesel produced by Sasol. Fuel properties are summarized below:

Fuel Property	Units	Diesel	FT
Specific Gravity		0.8705	0.7647
Cetane Number		41.5	74.8
Aromatics	wt %	38.4	< 1
Sulfur	ppm	404	< 1

The engine was a Caterpillar 1998 model year C12, a 12 liter DI, turbocharged engine. Four steady state modes were tested and results are reported below for the average changes. Note that these data are expressed in terms of g emissions/kg fuel, not the usual brake specific basis. While there was an average reduction in soot emissions with the FT diesel, in two of the modes, soot emissions increased. This may be a consequence of the higher cetane value, although as the authors point out, the reasons for this are not clear. Particle size distribution with the FT seemed to be somewhat narrower than with petroleum diesel. This may be the result of two trends. One is that the lower sulfur levels lead to fewer nucleation particles. The other is that with the overall lower emission level, there is less opportunity for agglomeration of large particles.

	Percent Change in Emissions Diesel → FT
HC	- 15
CO	- 15
NO$_x$	- 17
PM Total	- 24
PM VOF	- 43
PM Soot	- 13

Myburgh et al. [156] tested a FT diesel produced by Sasol and a low sulfur Japanese petroleum diesel in a HD vehicle. The engine was a 1998 model year Japanese 6.6 liter DI, naturally aspirated diesel with an inline injection pump, EGR, and an oxidation catalyst. Tests were run with and without the oxidation catalyst in place. Properties of the fuels are:

Parameter	Units	Low S Diesel	FT
Density	g/ml	0.8185	0.7680
Cetane Number		57.5	74
Aromatics	wt. %	21.2	0.1
Sulfur	ppm	29	< 1

The 13 mode emissions test is designed for an engine dynamometer, and the test was simulated on a chassis dynamometer to accommodate the program vehicle. Results are shown below for the non-catalyst configuration comparing the two fuels. In the absence of the catalyst, HC emissions increased with FT diesel, but the oxidation catalyst was more efficient with FT diesel, and the post-catalyst emissions were lower.

	Percent Change in Emissions LS Diesel → FT	
	Without Catalyst	With Catalyst
HC	+ 8	- 22
CO	- 22	- 60
NO$_x$	- 15	- 12
PM	- 18	- 21

Frank et al. [127] tested a Navistar 2001 model year DT466E engine commonly used in urban transit buses with a variety of fuels and with a number of different aftertreatment configurations. Engine displacement was 7.6 liters, and the engine was turbocharged with electronically controlled injection, and no EGR. A FT diesel and an ultra low sulfur diesel (ULSD) were tested in similar configurations. Properties are shown below:

Fuel Property	Units	ULSD	FT
Density	g/ml	0.8264	0.7833
Cetane Number		42.9	85.0
Aromatics	wt. %	20.2	0.8
Sulfur	ppm	28	1.2

Three aftertreatment configurations were tested – oxidation catalyst (DOC), continuously regenerating particulate trap (CRDPF) and DPF with EGR (EGR-DPF). The HD transient FTP test cycle was used, and the results are shown for the hot start portion which was run in all configurations.

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	Percent Change in Emissions ULSD → FT		
	DOC	CRDPF	EGR-DPF
HC	- 91	*	*
CO	- 89	*	+ 118[#]
NO$_x$	- 11	- 9	- 11
PM	- 23	*	*

* Values too low to evaluate differences
[#] Anomalous result with FT diesel

Generally, FT diesel reduced all emissions components. For some of the comparisons, the emissions were so low with both fuels that it was not possible to determine if there was a fuel effect. CO emissions increased when FT diesel was tested with the EGR-DPF system, but this result is suspect.

Yoshitomi et al. [165] tested three FT diesels with different volatilities along with a petroleum diesel and some blends in two HD engines. One engine was a 4 liter DI, turbocharged engine with common rail injection and DPNR aftertreatment system. The other was a 7.7 liter DI, turbocharged engine with a common rail injection system and DPF-NSR aftertreatment. Emissions were measured over the Japanese HD transient cycle, JE05. There were no differences in NOx emissions. PM emissions were lower by 30-60%. The less volatile FT fuels with lower T$_{90}$ had lower PM emissions.

The authors observed that engine design could be optimized for FT diesels. For instance, compression ratio could be reduced while still maintaining low emissions and good stable combustion. Efficiency would increase to be equal to petroleum diesel, while still maintaining low emissions.

Kuronen et al. [166] tested hydrogenated vegetable oil (HVO) along with two ultra low sulfur petroleum diesels. HVO is made in a refinery process that converts vegetable oil to paraffins, and has properties similar to FT diesel. Properties of the tested fuels are shown below.

Fuel Property	Units	HVO	ULSD-A	ULSD-B
Density	g/ml	0.779	0.839	0.839
Cetane Number		82.9	55.5	57.8
Aromatics	wt. %	< 0.02	18.4	22.1
Sulfur	ppm	< 1	4.5	< 10

Two urban buses were tested using the transient Braunschweig City Driving Cycle. One bus (A) had a model year 2006 7.3 liter engine with common rail injection and Urea-SCR aftertreatment. The other bus (B) had a model year 2006 8.9 liter engine with unit injectors, EGR and an oxidation catalyst.

Emission effects are shown below for each bus. Bus A was run with HVO and ULSD-A and Bus B was run with HVO and ULSD-B. HC emissions were extremely low, and no differences could be seen. CO reductions for Bus B were high with HVO, presumably a reflection of the oxidation catalyst in the aftertreatment system. Speciated emissions were measured, and there were no differences between the fuels for aldehydes or PAHs. Distribution of PM size was also similar for the fuels.

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	Percent Change in Emissions ULSD → HVO	
	Bus A	Bus B
HC	-	-
CO	- 5	- 50
NOₓ	- 7	- 9
PM	- 30	- 46

<table>
NOₓ above is NOx
</table>

SUMMARY OF FT EFFECTS

Almost all studies carried out with FT fuels show a reduction of emissions compared to petroleum diesel. There is a difference between LD and HD results with respect to NOx emissions. For HD diesel, NOx emissions were always improved with FT fuels, while the results for LD engines were mixed. This is the same conclusion reached by Alleman and McCormick [90] in their excellent review published in 2003. It is not known what individual properties of FT fuels caused the emissions benefits seen or why there is an apparent difference between LD and HD results.

G. DIESEL SUMMARY AND RESEARCH NEEDS

Significant data exist which relate diesel fuel properties and exhaust emissions, both for LD diesels and for HD diesels. In many cases, the conclusions are not consistent and may be contradictory. Possible reasons for disagreement among the published results include:

- Non-orthogonal design of fuel parameters. Results are presented in terms of one set of variables, but could be also explained in terms of a different set.
- Small numbers of vehicles or engines were tested and cannot be generalized to the entire fleet.
- Different test cycles were used, which may cause different fuel effects.
- Special blendstocks were splash blended which does not allow an analysis of the reasons for the effects, and which may be dependent on the base fuel used in the experiment.

The following table represents a summary of the current state of knowledge of the impact of fuel property changes on exhaust emissions.

	To Reduce Emissions, Make the Directional Changes Shown Below (Light Duty / Heavy Duty)						
	Density	Cetane	Aromatics/PAH	Sulfur	Back-End	Fatty Acid Esters	Fischer Tropsch
HC	↓/*	↑/↑	↑/↓	0/0	0/↑	↑/↑	↑/↑
CO	↓/*	↑/↑	↑/*	0/0	0/↑	↑/↑	↑/↑
NOₓ	*/↓	*/*	↓/↓	0/0	#/#	↓/↓	#/↑
PM	↓/*	↓/#	↓/↓	↓/↓	↓/↓	↑/↑	↑/↑

0 - No effect

* - Data are lacking to define effect

\# - Data exists, but effect is variable

For existing LD and HD diesel technology, a full statistical analysis of existing data would help develop an understanding of quantitative effects of fuel parameters on exhaust emissions. This would be an update of the work published by EPA in 2001. An important piece of this effort would be an analysis of the ability to determine unambiguously the impacts of density, cetane and aromatics on emissions. Much of the published data, with a few notable exceptions, has confounded these parameters. If the analysis cannot determine independent effects, then additional experimental data would be useful.

Additional research on Fatty Acid Esters and Fischer Tropsch liquids would be helpful to determine their effects. This research should not use splash blending to prepare fuels, but should blend fuels so that the contribution of these blendstocks can be tied to specific properties. A key question, especially for Fatty Acid Esters is why they reduce emissions.

There is a need for research on diesels with exhaust aftertreatment. Future diesel engines will almost certainly contain some form of aftertreatment. When the technology is developed and implemented, research should be carried out to determine the impact of fuel variables on engines and vehicles containing the new technology. There is some existing data with oxidation catalysts in LD diesels and with DPFs, but very little data with Urea-SCR and NSR systems.

Appendix III contains a compilation of the number of vehicles and fuels tested in programs that evaluated various fuel properties. As shown in the table, there is recent data for most parameters, with the possible exception of density (last data published in 2001) and cetane (last data published in 2004). If these parameters are considered important from a regulatory perspective, then additional data may be required before regulations are considered.

5. OFF-ROAD ENGINES AND VEHICLES

Off-road or nonroad applications consist of many uses and generally refer to internal combustion engines used for any application other than automobiles or trucks that travel on roads and highways. These include

- Lawn and garden equipment
- Small electric generators
- Construction equipment
- Mining equipment
- Recreational vehicles such as snowmobiles
- Farm vehicles and equipment
- Marine vessels, including personal watercraft
- Locomotives

For the purposes of this report, locomotives are not included. The list contains a wide variety of engine sizes, uses, duty cycles, and operating conditions. Most of the smaller engines are gasoline powered, and most of the larger ones are diesel powered.

As emissions from on-road vehicles have been reduced, off-road emissions have also been the subject of regulatory actions. Typically, emission control technology has advanced faster and been implemented sooner for on-road than for off-road applications. The consequence of this fact is that emissions from off-road sources are expected to grow much faster than from on-road sources.

In May 2004, EPA promulgated Tier 4 emission standards for off-road diesel engines [167]. These standards, which were coupled with standards controlling diesel sulfur levels, take effect over the years 2007-2015. In their analysis, EPA stated that they expected the controls to be catalyst based and enabled by the availability of 15 ppm sulfur diesel fuel.

In addition to promulgating new emission standards, EPA also promulgated new test procedures based on extensive data collection programs. The new tests involve a more accurate duty cycle and incorporate transient testing and cold start operation.

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The table below shows the national inventory for controlled pollutants, both with and without the Tier 4 off-road diesel emission standards. Without the Tier 4 standards, the relative size of off-road diesel emissions will grow as on-road mobile sources are controlled to a greater extent. With controls in place, the relative contribution of off-road diesel stays fairly constant.

National (48 state) Emissions Inventory for Land Based Non-Road Diesel [167]						
	1996		2020 (No New Controls)		2020 (With Tier 4 Controls)	
	Short Tons	% Mobile Sources	Short Tons	% Mobile Sources	Short Tons	% Mobile Sources
PM$_{2.5}$	186,507	47.2*	129,058	70.3*	50,065	47.9*
NO$_x$	1,564,904	12.1	1,119,481	22.2	677,420	14.7
VOC	220,971	2.7	97,513	2.5	19,372	2.1
CO	1,004,586	1.3	697,630	0.9	309,593	0.4
* PM$_{2.5}$ Percentages do not include gasoline vehicles.						

The figure below shows the relative sizes of the off-road PM$_{2.5}$ inventory for 1996 and 2020, with and without the Tier 4 standards promulgated in 2004. The size of the circles is proportional to the total inventory. With no new controls, off-road will continue to decline as a result of current programs being fully implemented. However, the yearly decline in emissions from the current standards diminishes over time, and by 2020, off-road emissions account for 70% of the total diesel mobile source PM$_{2.5}$ inventory. With the new Tier 4 standards, reductions in off-road sources keep pace with reductions achieved in on-road sources, and the relative contributions stay constant.

Diesel PM$_{2.5}$ Mobil Source Inventories
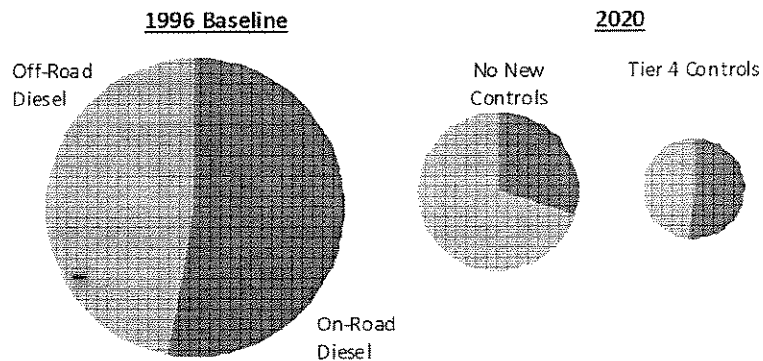
Federal emission standards for spark ignition off-road engines were proposed in 2007 and are expected to be phased in over the years 2009-2012 [168]. These new regulations are expected to result in significant changes in technology, including the introduction of catalytic aftertreatment systems, fuel injection, and systems to control evaporative emissions. The table below shows the contribution of spark

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ignition engines to the total mobile exhaust and evaporative emissions inventory. Emission standards limit the relative growth in emissions for this source relative to total mobile sources.

National (50 state) Emissions Inventory for Non-Road Spark Ignition Engines [168]						
	2001		2020 (No New Controls)		2020 (With Controls)	
	Short Tons	% Mobile Sources	Short Tons	% Mobile Sources	Short Tons	% Mobile Sources
VOC	3,113,628	39.2	2,061,845	41.1	1,567,325	34.7
CO	23,875,070	27.3	18,579,583	35.6	16,399,358	32.7
NO_x	490,365	4.0	266,903	5.6	194834	4.2
$PM_{2.5}$	56,214	12.4	53,466	22.4	48,377	20.7

While a great deal of data exists on the relationship between fuel properties and exhaust emissions for on-road vehicles, it is not clear that the data are relevant for off-road applications. There are major differences in design between on-road and off-road applications. For some applications, size and cost considerations make it difficult to adopt advanced technologies that are common on automotive engines. For example, virtually all automobiles use fuel injection to meter fuel, while current off-road engines use carburetors.

On the other hand, the duty cycles for off-road applications tend to be simpler and to include more steady state operation. The differences in duty cycles are reflected in the emission test cycles adopted by regulators.

The literature search conducted for off-road sources included research starting in 1990. A total of 106 abstracts were reviewed for relevance and 18 papers were purchased and read. Of these, seven papers described programs that measured fuel effects in spark ignition engines and eight papers described programs that measured fuel effects in compression ignition engines. None of the research reported in the literature reported on the independent effect of individual fuel parameters. Where single properties such as ethanol concentration were varied, it was generally done in a way that changed many properties simultaneously.

A. SPARK IGNITION ENGINES

The published literature on fuel effects on emissions from off-road spark ignition engines and vehicles has been limited to small engines used for lawn and farm equipment or for snowmobiles. These engines were all manufactured to operate on gasoline, and some were modified to operate on LPG. As discussed above, none of the studies evaluated specific chemical or physical fuel characteristics in a designed experiment. Either materials were splash blended into fully formulated fuels, or else two or more fully formulated fuels were compared.

OXYGENATES

Ethanol use was studied in a number of different engines types, and forms the largest body of research in the off-road spark ignition area. White et al. [169] tested two snowmobile engines with three fuels – base gasoline, splash blended gasohol and an aliphatic gasoline. Both engines were two cylinder 2-stroke carbureted models having a displacement of around 450 cm^3. Neither one had a catalyst. The test cycle consisted of 5 steady state modes on a dynamometer. Lubricants were also tested. Results comparing the ethanol fuel and base gasoline with a common lubricant are shown below:

Percent Change (based on g/kW-hr) Base Gasoline → Gasohol		
	Engine	
	Polaris	Arctco
HC	- 16	+ 5
CO	- 9	- 6
NO_x	+ 1	+ 6
PM	- 24	- 3
Benzene	- 10	*
1,3 Butadiene	+ 7	*
Formaldehyde	+ 5	*
Acetaldehyde	+ 555	*
Specific Reactivity ($g\ O_3$/g HC)	+ 3	*
* Not tested		

The results for the Polaris engine are consistent with an engine running rich, where adding an oxygenate will lean out the mixture and reduce emissions of unburned and partially burned material. The small response of the Arctos engine was not explained by the authors, except to point out that it was a water cooled engine. No statistical analysis was presented to evaluate whether the results were significant.

Bresenham and Reisel [170] studied splash blended ethanol-gasoline mixtures in two models of small utility engines. Three engines were tested. Two were Briggs and Stratton 12.5 hp (9.3 kW) slide valve engines, and the third was a 12.5 hp (9.3 kW) Kohler overhead valve engine. All three engines were carbureted. The test cycle was SAE J1088, which is a series of six steady state conditions. Five are loaded at 85% of rated speed and the sixth is a no-load idle mode. Four fuels were tested – a HC base and splash blends with 10%, 25% and 50% ethanol. No composition data was provided for the base blend.

All three engines started out rich and became progressively leaner as the concentration of ethanol increased. One of the engines operated just lean of stoichiometric at 50% ethanol, while the other two stayed slightly rich. Results are shown below:

Percent Change (based on g/kW-hr) Base Gasoline → Ethanol Blends									
	HC			CO			NO_x		
	10% EtOH	20% EtOH	50% EtOH	10% EtOH	20% EtOH	50% EtOH	10% EtOH	20% EtOH	50% EtOH
Engine 1	- 8	- 22	- 72	- 19	- 50	- 92	+ 12	+ 44	+ 85
Engine 2	- 11	- 37	*	- 21	- 62	*	+ 36	+ 152	*
Engine 3	+ 4	- 18	- 40	- 2	- 43	- 74	- 10	+ 84	+ 211
* Not tested									

These results are consistent with the stoichiometry reported for the engine. As more ethanol was added, HC and CO emissions decreased and NO_x emissions tended to increase. It is interesting to note

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that the changes in the sum of HC and NO_x, the regulated measure of emissions, are very small. No statistical analysis of the results was presented.

Varde and Clark [171] tested 10% and 85% ethanol blends in a single cylinder carbureted small industrial (Class II) engine. Adjustments were made in spark timing, carburetor jets and stoichiometry control to accommodate the ethanol blends. The actual stoichiometry was not reported.

Emissions were measured at four loads and at two spark timings – standard and maximum brake torque. Results were shown graphically. CO and NOx emissions tended to decrease as ethanol concentrations increased, while HC emissions tended to increase. No statistics were reported. It was suggested that the high heat of vaporization lowered the combustion chamber temperatures and could help explain the HC and NO_x effects.

Martinez and Ganji [172] tested a single cylinder utility engine with a number of ethanol blends. The engine was a 2.5 hp Honda, 83 cm^3 displacement with slide valves, a carburetor and fixed timing. It is typical of engines used in yard applications and pump and compressor sets. Five fuels were tested, comprising pure gasoline, pure ethanol, and 10%, 20% and 40% ethanol blends. Load, stoichiometry and spark advance were varied.

At equivalent power output, ethanol blends reduced emissions of NOx and CO by up to 60%. HC emissions were lower at low output, but were the same at higher outputs. No statistics were reported for the results.

Merritt and Netemeyer [173] tested a fuel with ETBE in three small engines – a four stroke overhead valve engine (160 cm^3), a four stroke side valve engine (188 cm^3) and a two stroke engine (60 cm^3). The four stroke engines complied with EPA 2007 regulations and the two-stroke engine complied with EPA 2004 regulations. These were all relatively high volume engines used for lawn and power equipment. A fuel with ETBE (2% oxygen) was compared to a non-oxygenated fuel. The ETBE had very low sulfur (1 ppm versus 64 ppm) and olefins (1% versus 9%) and no aromatics (versus 29%). The CARB SORE (Small Off-Road Emissions) emissions test was used. It consists of six steady state modes. Results are shown below:

Percent Change (based on g/kW-hr) Base Gasoline → ETBE Gasoline			
	Engine		
	Four Stroke		Two Stroke
	Side Valve	OHV	
HC	- 2.4	- 6.6	- 9.4
CO	- 13.8	- 13.2	- 22.7
NO_x	+ 2.0	+ 3.0	0
PM	*	*	- 28.9
Benzene	- 88	- 82	- 83
1,3 Butadiene	- 32	- 24	- 42
Formaldehyde	+ 32	+ 25	+ 48
Acetaldehyde	+ 2	+ 98	+ 208
Total Toxics	- 53	- 45	- 43
Ozone Forming Potential	- 2.1	- 4.4	- 29.7
* Not tested			

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Since there were a number of property changes, it is not possible to ascribe emissions effects to the use of ETBE. However, some changes may have been due to the addition of the oxygenate. No statistical analysis was provided.

OTHER GASOLINE PROPERTIES

A number of studies evaluated "clean" gasolines. White et al. [169], in the program described above, tested a snowmobile engine with a base gasoline and an aliphatic gasoline.

A comparison of the properties of the two fuels is shown below. Properties not shown were generally equivalent.

Fuel Property (Units)	Reference Gasoline	Aliphatic Gasoline
RVP (psi)	8.9	9.4
Aromatics (Vol. %)	27	1.6
Benzene (Vol. %)	0.17	0.0
T_{90} (°C (°F))	152 (306)	122 (252)

Results comparing the aliphatic and base gasolines are shown below, for a common lubricant:

Percent Change (based on g/kW-hr) Reference Gasoline → Aliphatic Gasoline	
	Polaris Engine
HC	+ 33
CO	+ 2
NO_x	+ 12
PM	+ 47
Specific Reactivity (g O_3/g HC)	- 25

The aliphatic fuel had substantially higher HC and PM emissions. The authors did not attempt to explain these effects except to note that the aliphatic fuel had poor combustion quality as evidenced by frequent misfire. Fuel consumption increased and maximum power was reduced. It is not clear from the fuel properties why these effects were seen.

Mayer et al. [174] tested two Briggs and Stratton engines used commonly in yoke mowers in Swiss agriculture. One was a two cylinder engine having a displacement of 479 cm^3 and rated at 9.2 kW. The other was a single cylinder engine with 399 cm^3 displacement and rated at 8.1 kW. Both complied with California's 1996 emission limits. The test cycle was ISO8178 Type G, which measure emissions at six steady state conditions and calculates a weighted average. Both engines were retrofitted with an emission control system that included a three way catalyst and adjusted carburetion to produce a leaner mixture.

Two fuels were tested, a standard Swiss gasoline and a non-aromatic "alkylate" gasoline. The authors did not present actual properties of the test fuels, except to say that aromatics, sulfur and olefins were typically extremely low for the alkylate fuel.

Emission results comparing the two fuels are shown below for tests with and without the catalyst.

Percent Change (based on g/kW-hr) Reference Gasoline → Alkylate Gasoline		
	With Catalyst	Without Catalyst
HC	0	- 1
CO	- 22	- 3
NO$_x$	- 29	- 34

PM emissions were measured and were not affected by the fuels. No statistics were reported for any of the results. The authors did not attempt to explain any of the results, especially the different effects for CO when measured with and without a catalyst.

In a program described above, Merritt and Netemeyer [173] tested a "Green" fuel in three small engines – a four stroke overhead valve engine (160 cm^3), a four stroke side valve engine (188 cm^3) and a two stroke engine (60 cm^3). The non-oxygenated Green fuel had very low sulfur (1 ppm versus 64 ppm) and olefins (1% versus 9%) and no aromatics (versus 29%). Results are shown below:

Percent Change (based on g/kW-hr) Base Gasoline → Green Gasoline			
	Engine Type		
	Four Stroke		Two Stroke
	Side Valve	OHV	
HC	+ 9.3	+ 2.7	+ 1.3
CO	- 10.3	-4.5	+ 1.4
NO$_x$	+ 0.65	+2.49	- 25.0
PM	*	*	- 4.8
Benzene	- 80	- 88	- 24
1,3, Butadiene	+ 28	0	- 93
Formaldehyde	+ 41	+ 17	+ 42
Acetaldehyde	+ 2	- 10	+ 1
Total Toxics	- 41	- 57	- 51
Ozone Forming Potential	+ 21	- 3	- 18
* Not tested			

The authors did not discuss possible reasons for the effects seen here, although it's clear that the dramatic reduction in benzene emissions is a result of the lack of any aromatic compounds in the green fuel. No statistical analysis was presented.

Sun [175] tested four engines typically used for commercial lawn and garden equipment. All were spark ignited, air-cooled, carbureted engines ranging in hp from 5 to 18. They were modified to run on LPG with feedback control at the same stoichiometry as with gasoline (lambda = 0.83). The test cycle was the six mode SAE J1088 test. Emission results are shown below for the four engines and two fuels.

	Percent Change (based on g/kW-hr) Gasoline → LPG			
	Engine 1	Engine 2	Engine 3	Engine 4
HC + NO$_x$	- 19	- 36	- 69	- 13
CO	- 42	- 39	- 67	- 55

The engines had much lower emissions when running on LPG. The authors did not try to explain the differences.

B. COMPRESSION IGNITION ENGINES

Compression ignition engines tend to be larger than spark ignition engines, and are common in agriculture, industrial and construction applications. In terms of research programs reported in the literature, most of the comments made above with respect to spark ignition engines apply to compression ignition engines as well. Few, if any, literature reports discuss independent property variations in diesel fuel applications. A number of projects measured emissions using methanol and/or ethanol, which are unlikely to be used in the near terms in commercial applications.

ALCOHOLS

Although alcohols are generally not miscible in diesel fuel, have poor cetane quality, and require engine modifications for use in compression ignition engines, a number of studies have been carried out on use of alcohols.

Hemsley et al. [176] tested methanol in three modified yard-hosteler engines. Cummins CT8.3 diesel engines were replaced with DDC-71TA methanol engines. The methanol engines had high compression ratios (23:1), and catalytic converters. Performance for the two engines was roughly equal. Methanol fuel was mixed with 1.5% Avocet™, a combustion improver. The engine did not require a glow plug to initiate combustion because of the high compression ratio and ignition improver.

Although the main focus of this project was to demonstrate the potential for methanol fuel, emissions were also measured. The methanol fuel reduced all emissions components by large amounts - NOx by 28%, PM by 81%, HC by 87% and CO was totally eliminated. It is not clear how much of this reduction was due to the presence of a catalyst and how much was due to the use of methanol.

Merritt et al. [177] tested three off-road HD John Deere diesel engines with ethanol blends. The engines had displacements of 8.1, 6.8 and 12.5 liters, and were all certified to Tier II EPA standards. The injection systems were common rail, rotary pump and unit injector respectively. Four fuels were tested – base diesel and ethanol blends of 7.7%, 10% and 15% by volume. Three proprietary additives were used to keep the ethanol miscible with diesel. The 8-mode EPA test procedure was used for emissions measurements.

PM emissions decreased by 13-30% with ethanol in the three engines. CO emissions decreased up to 15% in the 8.1 and 12.5 liter engines. In the 6.8 liter engine, CO increased as much as 23%. NOx emissions were reduced between 5-9% in the 6.8 liter and 12.5 liter engines. NOx emissions increased a small amount in the 8.1 liter engine. Emissions of acetaldehyde increased with ethanol in all three

engines (27%-139%). Emissions of benzene and 1,3 butadiene were reduced in all engines with the use of ethanol. The authors did not discuss the anomalous CO results. Statistics were not presented.

Kumar et al. [178] tested ethanol-diesel microemulsions using up to 23% ethanol with 17% ethyl acetate as a stabilizer. Ethanol reduced CO emissions at high load, but increased CO emissions at low loads. HC emissions also increased over the entire load range. NOx emissions were mixed.

OTHER OXYGENATES

Dan et al. [179] tested a 4-stroke single cylinder high speed marine diesel with diesel/DME (di-methyl ether) blends. The engine had a compression ratio of 17.7, a jerk type injection pump, and a displacement of 0.638 liter. Three fuels were tested – 100% marine diesel, a 70% diesel/30% DME mixture and a 60/40 mixture. NOx emissions were 15-25% lower for the mixtures. The authors speculated that the volatile DME increased the pre-mix combustion, causing heat release to be extended and peak temperatures to be reduced. Smoke emissions were also reduced with DME mixtures.

HYDROCARBON FUELS

Nord and Haupt [180] tested a Valmet diesel engine, commonly used for farm machinery such as tractors and harvesters. It was a six cylinder turbocharged engine with 6.6 liter displacement and a rotary fuel injection pump. Two fuels were tested. One was a Fischer Tropsch diesel made by Eco-Par™ and the second was a Swedish EC-1 diesel. The two fuels had similar compositions except that the EC-1 had slightly higher density (0.815 versus 0.799 g/cm^3) and was more volatile (T_{50} of 230°C versus 253°C). Emissions were measured over the ISO 8178 test procedure. Emissions of NOx were reduced 7%, HC emissions were reduced 15% and CO was reduced 3%. Emissions of the toxics benzene, 1,3 butadiene, formaldehyde and acetaldehyde were also lower with the Fischer Tropsch fuel.

Frame et al. [181] tested a military 6.5 liter HD engine using hot start transient dynamometer testing with the FTP and a nonroad San Antonio Transit cycle (SAT). Two fuels were tested. One was a low sulfur conventional diesel and the other was a synthetic JP-5 fuel made using the Fischer Tropsch process by Syntroleum. Fuel properties are summarized below.

Test Fuel Properties		
Fuel Property (Units)	Low Sulfur Diesel (LSD)	Synthetic JP-5
Sulfur (ppm)	370	< 1
Aromatics (Vol. %)	30.9	0.9
Cetane Number	47.9	69.3
T_{50} (°C, (°F))	260 (500)	220 (428)
Density (g/cm^3)	0.845	0.765

A comparison of emissions is shown below for the two test cycles.

Percent Change (based on g/kW-hr) LSD → FT Diesel		
	FTP Cycle	SAT Cycle
HC	- 62	- 72
CO	- 47	- 60
NO_x	- 13	- 15
PM	- 55	- 52

The changes in emissions are generally in line with the properties of the fuels. PM, for instance, would tend to be lowered by reductions in sulfur, density and aromatics (especially PAHs). No statistical analysis was reported.

Matthews et al. [182] tested a model year 2001 Cummins ISB 190 engine from a Gradall model XL3100 grader. No engine details were provided except that the engine did not have any aftertreatment. The test cycle was the TxDOT Boom Excavator Cycle. Two fuels were tested. One was a standard low sulfur diesel, and the other was a Texas Low Emissions Diesel (TxLED). Properties of the fuels are shown below.

Test Fuel Properties		
Fuel Property (Units)	Texas LSD	TxLED
Sulfur (ppm)	377	2.5
Aromatics (Vol. %)	33.4	5.9
Cetane Number	46.8	50.5
T_{50} (°C, (°F))	262 (504)	269 (516)
Density (g/cm^3)	0.8419	0.8454

Emissions comparisons are shown below. All differences are statistically significant (95% CL).

Percent Change (based on g/kW-hr) Texas LSD → TxLED	
HC	- 38
CO	- 12
NO_x	- 6
PM	- 18

Birch and Kubesh [183] modified a diesel engine to run on LPG. The diesel engine was a John Deere PowerTech 4.5 liter engine used in a model 4510 tractor commonly used for park and right of way maintenance. The modifications included adding spark ignition, a new fuel system to accommodate LPG and control stoichiometry, and an oxidation catalyst. Although torque and thermal efficiency were reduced by about 5% with LPG, emissions were substantially lower on the ISO 8178 test cycle, as shown below. The measure of emissions used by the authors was HC+NO_x because this is the form of the emission standard.

Percent Change (based on g/kW-hr) Diesel → LPG	
HC + NO$_x$	- 44
CO	0
PM	- 92

The LPG engine met 2008 EPA Tier 3 emission standards. The large reduction in HC+NO$_x$ was driven by a reduction in NO$_x$. This is understandable given that diesel emissions are typically very low in HC and CO and high in NO$_x$. A reduction in HC and CO would therefore not be expected to be large if there was one at all.

C. OFF-ROAD SUMMARY AND RESEARCH NEEDS

Off-road engines and vehicles are important contributors to mobile source emissions in the United States. As emissions from on-road vehicles continues to decline, the relative importance of emissions from off-road sources becomes more important and is being subject to control as well. Under current programs, off-road sources are predicted to contribute as much as 30-50% of the total in 2020.

Not much research has been carried out exploring the impact of fuel quality on exhaust emissions from off-road vehicles and equipment. The research that has been published has focused on understanding the impact of blendstocks that are splash blended into fully formulated fuels. This fact, coupled with the multitude of applications for off-road equipment, makes it difficult to predict the impact of fuel properties on exhaust emissions from off-road applications.

SPARK IGNITION ENGINES

Most of the research on spark ignition engines has evaluated oxygenates, especially ethanol, in a splash blended environment. Results are consistent with engines that were running rich and were leaned out by the addition of oxygen.

As part of their recent rulemaking proposals for future emission standards, EPA stated that they expected to see major technology improvements in off-road gasoline engines over the next 4 years. The changes that EPA expects include feedback control of stoichiometry and catalytic aftertreatment. These changes suggest that future technology might have different responses than existing off-road technology.

COMPRESSION IGNITION ENGINES

Most of the research on compression ignition sources has evaluated fully formulated diesel fuels in a way that the effects of individual properties could not be determined. Some studies also evaluated alcohols such as ethanol and methanol. The likelihood of these alcohols gaining widespread use in commercial diesel fuel is fairly low.

Tier 4 emission standards for off-road diesel engines were promulgated by EPA in 2004, and will be implemented over the years 2008-2015. EPA expects these standards to be met by adoption of new technology, including catalytic aftertreatment. This was one of the main reasons that off-road diesel fuel will have a maximum sulfur level of 15 ppm. It is difficult to predict how emissions from these technologies will respond to fuel properties.

RESEARCH NEEDS

More stringent emission standards have recently been adopted or proposed by EPA for off-road sources. It is expected that the new standards will result in development and implementation of new technology such as catalytic aftertreatment and feedback control of stoichiometry. Since off-road sources are expected to continue to be a major source of emissions in the future, it would be worthwhile to develop a substantial database on the relationship between fuel properties and emissions. There is a

major benefit to having one fuel distribution system and not require specialize fuels for off-road applications. Therefore, development of such a database should center on the current or expected properties of gasoline and diesel fuels.

Considering that the current database is sparse, considerable thought would have to be given to allocation of resources among:

- spark ignition and compression ignition applications
- engine types within each major area

Appendix III contains a compilation of the number of vehicles and fuels tested in programs that evaluated various fuel properties. The table reflects the paucity of data for off-road sources, especially considering the large number of different applications.

APPENDIX I

Statement of Work: CRC E-84

Review of Prior Studies of Fuel Effects on Vehicle Emissions

The Coordinating Research Council (CRC) is seeking a comprehensive review of published studies of fuel property effects on vehicle exhaust emissions. The study should cover gasoline light-duty vehicles and diesel light and heavy-duty vehicles. CRC will also consider as an option a review of fuel effects on non-road emissions. The intent of the study is to update previous reviews conducted by Koehl et al. (1) on light-duty gasoline and by Pedley et al. (2) on heavy-duty diesel. Highest priority should be given to studies published after these reviews and to vehicle technologies that make up the bulk of the current and future US vehicle fleet.

While the highest priority should be given to studies covering US vehicles, fuels and emission testing procedures, relevant studies from Europe, Japan and other regions should also be included. Emphasis should be on published studies using established government/industry emission measurement procedures simulating in-use vehicle operation and with well designed test fuel matrices with independent variation in one or more fuel property that allow individual fuel property effects to be evaluated.

Fuel properties should include regulated properties or those covered in the reviews of Koehl et al. and Pedley et al. For gasoline, key fuel properties include RVP, sulfur, distillation properties, oxygenate, aromatics, benzene, and olefins and for diesel, cetane - both natural and additized, aromatics, density, and distillation. Other properties may be included if experimental information indicates that they have a significant impact. The impact of vehicle technology on fuel effects including emission control technology should also be considered. The study should include mass emissions of criteria pollutants NMHC, NO_x, CO and PM, and HC speciation effects including air toxics and ozone formation potential.

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1) Koehl W.J., J. D. Benson, V. Burns, R. A. Gorse, A. M. Hochhauser and R.1 Reuter, 1991, "Effects of Gasoline Composition and Properties on Vehicle Emissions: A Review of Prior Studies – Auto/Oil Air Quality Improvement Research Program," SAE 912321.
2) Lee R., J. Pedley, and C. Hobbs, 1998, "Fuel Quality Impact on Heavy-Duty Diesel Emissions: - A Literature Review," SAE 982649.

APPENDIX II
List of Acronyms

A/F – Air Fuel Ratio (mass)

AQIRP – Auto/Oil Air Quality Improvement Research Program

ARB – (California) Air Resources Board, sometimes referred to as CARB

ASTM – ASTM International, voluntary standards development organization; formerly American Society for Testing and Materials

CO – Carbon monoxide

CRC – Coordinating Research Council

DECSE – Diesel Emissions Control – Sulfur Effects Project

DEE – Di-ethyl ether

DI – Direct Injection

DMM – Di-methoxy methane

DPF – Diesel Particulate Filter

ECE – Economic Commission for Europe (emissions test cycle)

EGR – Exhaust Gas Recycle

EPA – United States Environmental Protection Agency

EPEFE – European Program on Emissions, Fuels and Engine Technologies

ETBE – Ethyl *tertiary*-butyl ether

FAE – Fatty Acid Ester

FT – Fischer Tropsch

FTP – Federal Test Procedure (for emissions)

GDI – Gasoline Direct Injection

GTL – Gas-to-Liquid

HC – Hydrocarbons

HCCI – Homogeneous Charge Compression Ignition

IDI – Indirect Injection

JCAP – Japanese Clean Air Program

JCME – Jatropha curcas methyl ester

MPI – Multi-Point Injection

MTBE – Methyl *tertiary*-butyl ether

NBA – Non-Benzene Aromatics

NEDC – New European Driving Cycle

NMHC – Non-methane hydrocarbons

NMOG – Non-methane organic gases

NO_x – Oxides of nitrogen

NREL – National Renewable Energy Laboratory (DOE)

NS – not statistically significant

NSR – NOx Storage Reduction

OBD – On-Board Diagnostics System

PM – Particulate Matter

POME – Palm oil methyl ester

PPEE – Pongamia Pinnata ethyl ester

PPME – Pongamia Pinnata methyl ester

RSME – Rapeseed methyl ester

SAE – Society of Automotive Engineers

SIDI – Spark Injection Direct Ignition

SOF – Soluble Organic Fraction or particulate emissions

TAME – *tertiary*-amyl methyl ether

TLEV – Transitional Low Emissions Vehicle

TOG – Total Organic Gases

TWC – Three way catalyst

Urea-SCR – Urea based Selective Catalytic Reduction

APPENDIX III
Summary of Fuels and Vehicles Database

An Excel spreadsheet was prepared, which contains summary information that was used in preparing this report. For every data and review reference cited in this report, the following information has been tabulated:

Paper Number (typically SAE number)

Main author

Data paper or review paper

Fuel parameters studied

Number of fuels tested

Was PM measured (diesel only)

Number of vehicle or engines tested

Country or region represented by fuels/vehicles

Comments as appropriate

Full citation

The spreadsheet is organized so that it can be sorted easily to determine, for instance, all the references that tested one or more fuel parameters. It is available from CRC (www.crcao.org).

The three tables shown below contain summary information for the gasoline, diesel and off-road areas. They are intended to summarize the general size of the database, and to show when the most recent data was collected. In studies that used a factorial design, all fuels were used to determine the response of all design parameters. In a number of studies, other statistical designs were used, and not all fuels were used to determine the response of all the parameters. Therefore, the tables below might contain some values that are somewhat high. .A more detailed analysis of the references would be required to determine how many emissions tests were conducted for each parameter.

Data Summary - Gasoline Studies			
Property	# Studies	Vehicles	Fuels	Most Recent Publication Date
Sulfur	36	360	307	2003
Aromatics	35	334	346	2007(Most recent work covers GDI)
Olefins	21	236	215	2007 (Most data >9 years old)
RVP	14	289	142	1999
Mid-fill Back-end	33	373	430	2007 (19 studies examined both back-end and mid-fill)
Ethers	33	382	345	2007
Ethanol	18	214	177	2007

Data Summary - Diesel Studies				
Property	**LD/HD**	**# Studies**	**Vehicles**	**Fuels**	**Most Recent Publication Date**
Cetane	L	15	86	267	2004
	H	13	63	205	2007
Density	L	11	72	194	2001
	H	6	44	132	2000
Aromatics	L	16	109	279	2007
	H	17	90	257	2007
Sulfur	L	13	41	140	2007
	H	12	34	93	2005
Back-end	L	14	81	200	2007
	H	9	51	77	2007
Oxygenates	L	11	19	107	2007
	H	15	33	128	2007
Fischer-Tropsch	L	14	25	77	2007
	H	13	20	77	2007

Data Summary - Diesel Studies				
Property	**Gasoline/ Diesel**	**# Studies**	**Vehicles**	**Fuels**	**Most Recent Publication Date**
Oxygenates	G	5	10	18	2006
	D	4	9	13	2007
Fischer-Tropsch	D	2	2	4	2004
Other	G	4	11	10	2005
	D	2	2	4	2005

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APPENDIX IV
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